TRANSFER AND STORAGE OF VIBRATIONAL ENERGY IN LIQUIDS: LIQUID CARBON MONOXIDE AND ITS SOLUTIONS WITH ARGON

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Liquid carbon monoxide and its solutions with argon in a five order of magnitude concentration range were vibrationally excited by pumping with a blackbody source. Infrared fluorescence decay from the excited carbon monoxide was used to explore the storage and transfer of vibrational energy in this system. In the limit of the infinitely dilute solution the storage time, 18 ns, is determined by IR spontaneous emission. For concentrations in the range 0.01–1 mole % this radiation tends to be trapped by CO self-absorption and the lifetime of the vibrational excitation lengthens. We apply a simple model to interpret this lifetime behavior. Neat carbon monoxide stores vibrational energy for 1 s. Here radiation trapping is so effective that vibrational energy is lost essentially by non-radiative processes. The 1 s lifetime allows a useful limit to be placed on the vibration to translation and rotation rate of relaxation of excited CO by its neighbors.

1. Introduction

Vibrationally excited nitrogen or carbon monoxide is unusually stable to collisional relaxation. The stability is so great in fact, that it has not been possible to measure the decay of N$_2^*$ or CO$^*$ (the asterisk labels the $v = 1$ level) by vibration to translation and rotation (V–T, R) processes except at high temperatures. However, the addition of other molecules to N$_2^*$ or CO$^*$ can open up vibration to vibration (V–V) channels and then relaxation often proceeds rapidly.

Even in the high densities of the liquid state it has been difficult to set limits on V–T, R relaxation processes. We were the first to study [1] liquid nitrogen and other work followed [2–4]. We have recently shown [5] that the V–T, R relaxation time constant in carefully purified liquid nitrogen is at least 100 s. Addition of other molecules even at the ppb (part per billion) level can shorten this lifetime considerably [2,4,6]. Studies of CO$^*$ relaxation in the neat liquid [7] and dissolved in nitrogen [2–4] and placed in rare gas matrices [8,9] have also been reported.

Our purpose in this work has been to determine what effect the liquid environment has on vibrational relaxation processes. In this way we can test theoretical models which try to describe energy transfer in liquids. We also want to understand the limits of these unusual systems for storing vibrational energy. There is the possibility that if they are suitably pumped these liquids can be used to drive new laser systems and to direct chemical reactions.

In this paper we direct our attention to liquid carbon monoxide and its solutions with argon. Because CO$^*$ can fluoresce brightly it can be conveniently monitored for energy transfer studies. In his pioneering studies begun before chemists were introduced to lasers, Millikan [10] showed how to pump and measure the emission of CO$^*$ in order to reveal collisional relaxation processes. We have borrowed his technique for our study.

Here we vary the CO concentration in liquid argon over 5 orders of magnitude. In dilute solutions we measure the radiative lifetime of CO$^*$ and compare our result to theoretical predictions. At moderate CO concentrations (between $\approx 0.01$ and $\approx 1.0$ mole %) we find that radiation trapping lengthens the lifetime of CO$^*$ in a qualitatively predictable manner. At high
CO concentrations the lifetime deviates from the pattern set by the intermediate CO concentration solutions and levels off indicating that a relaxation pathway other than fluorescence has become important. This pathway is the relaxation of CO* by collisions with CO through the V–T,R channel. The measured 100 mole % CO concentration solution allows us to set an upper limit for this process.

2. Experimental and results

Great care was taken to ensure the purity of the Ar–CO solutions. The Ar was supplied by Matheson gas company with a stated purity of 99.9995% ("Matheson Purity"). Before being used this gas was passed through a column cooled to dry ice temperature containing Linde type 4A molecular sieve in order to reduce the level of H₂O and CO₂. Two brands of CO were used. Airco "Research Grade" and Scientific Gas Products "Research Grade", both with stated purity of 99.99%. Slower relaxation rates for the high CO concentration (greater than 1 mole %) solutions were obtained with the Airco "Research Grade" CO indicating a greater purity. Before use, it too was passed through a column containing Linde type 4A molecular sieve but cooled to liquid N₂ temperature. This was done to reduce not only H₂O and CO₂ levels but to try to eliminate hydrocarbons.

Low concentration (less than 0.3 mole % CO) solutions were prepared by filling the cell, at room temperature, to a predetermined pressure of CO after which the dewar was cooled to liquid Ar temperature and purified Ar condensed on top of the CO. Concentrations were estimated by knowing the volume of the liquid cell and the pressure of the CO which was assumed to behave as an ideal gas. For dilute samples, below 0.03 mole % CO, concentrations were checked by taking an infrared spectrum of the liquid sample. For more concentrated solutions the concentrations were confirmed by evaporating the sample and collecting a portion into a 10 cm gas cell and taking an infrared spectrum of the gas. High CO concentration solutions, above 1.0 mole % CO, were prepared by condensing CO in the sample cell and then condensing Ar on top of the CO. All concentrations are believed to be accurate to within 10%. From monitoring the vapor pressure of the samples the temperature was estimated to be 85 ± 1 K.

Fig. 1. Schematic representation of the experimental apparatus.

We use virtually the same optical system that was designed and built for our investigation of the liquid N₂–CO solutions [5]. A schematic of this apparatus is shown in fig. 1. A cylindrical elliptical mirror focuses the radiation of a globar through a window on the dewar and into a cryogenic cell containing the solution of argon and CO. All of the windows on the dewar and the cell are sapphire. In order to observe the radiative decay of the solution, the chopper (C) was activated to block the pump light from the globar. Emission was collected from a hole in the bottom of the cell, focused by a mirror (S), and sent through a Perkin–Elmer model 210-B monochromator with a grating blazed at 3.75 μ and set for the emission frequency of CO* (~2100 cm⁻¹). A lithium fluoride plug at the bottom of the cell helps reduce the amount of emission from CO* lost by absorption by CO in this portion of the cell. The signal was detected by an InSb photovoltaic detector cooled to 77 K. The signal from the detector was amplified and sent into a Fabri-Tek 1974 signal averager. A pulse taken from the chopper was used to trigger the signal averager. Typically between 250 and 1050 decays were averaged and then recorded on the strip chart. An aver-
Fig. 2. Typical decay signal from 0.0025 mole % CO solution. This decay is the sum of 250 scans.

aged decay for the 0.0025 mole % CO solution is shown in fig. 2.

The observed vibrational relaxation rate behavior with CO concentration is shown in fig. 3. The data are presented on logarithmic scales because the CO concentration was varied over 5 orders of magnitude. Below 0.01 mole % CO, the rate is essentially invariant with concentration with a value of $55 \pm 2 \text{ s}^{-1}$. At concentrations between 0.01 and 1.0 mole % CO radiation trapping by unexcited CO molecules becomes important and the observed rate decreases sharply.

Above 1.0 the rate begins to level off achieving its slowest value of $1.1 \pm 0.1 \text{ s}^{-1}$ for the 100 mole % CO solution. By replacing the liquid Ar coolant with liquid N$_2$ the 0.0025 mole % CO solution was frozen to about 80 K and a lifetime of $66.8 \pm 2 \text{ s}^{-1}$ observed and represented by the open circle in fig. 3.

In order to take fluorescence spectra the chopper was removed from in front of the globar and placed at the entrance to the monochromator. The emission was chopped at 13 Hz and the signal from the pre-amp fed into a lock-in amplifier. The spectra were recorded on a strip chart as the monochromator was scanned. A spectrum at 8 cm$^{-1}$ resolution for a dilute CO solution is shown by the solid line in fig. 4. Scattered light absorbed in part by CO distorts the background and obscures the fluorescence. This scattered light contribution was determined by making a doped Ar–CO sample so that all fluorescence was quenched. This solution was saturated with CO$_2$ which provides efficient radiationless pathways for the system to relax [6]. The scattered light spectrum from this doped solution is copied onto fig. 4 as the dotted line. It is subtracted from the undoped spectrum (the solid line) to give the low concentration emission bands of CO$^*$ (the dashed line). This emission spectrum is presented in the upper part of fig. 5 in a format to be discussed later. It will be used to model the self-absorption phenomena.

The intensity of the fluorescence increases with CO concentration up to $\approx 0.3$ mole % CO. Above this
concentration the intensity decreases such that emission from the 100 mole \% CO solution is weak. This we believe is in part the result of self-absorption of the fluorescence near the exit window (around the LiF plug) where the sample is unexcited by the globar radiation and also the result of non-radiative relaxation of the CO\(^{\ast}\) by either CO or impurities. Self-absorption is so severe at 100 mole \% CO that emission can only be observed at 1980 ± 30 cm\(^{-1}\). This represents a shift of the emission peak by ≈160 cm\(^{-1}\).

While the bandshape of the CO\(^{\ast}\) fluorescence undergoes dramatic distortion with CO concentration the absorbance profile remains invariant. An absorbance spectrum for a dilute CO solution is shown at the bottom of fig. 5.

3. Discussion

We interpret the lowest concentration rate shown in fig. 3 as the radiative relaxation of CO\(^{\ast}\) uninhibited by self-absorption effects. Its value is \(k_{\text{CO}^{\ast},\text{rad}} = 55 \pm 2\ \text{s}^{-1}\). This radiative rate can be calculated from the measured liquid state integrated absorption coefficient or by correcting the gas phase lifetime for solution effects.

The lifetime is related to the integrated absorption coefficient by the relationship [11]

\[
k_{\text{CO}^{\ast},\text{rad}} \approx 8\pi c \bar{\nu}^2 n_1^2 \int_{\text{band}} e(\nu) \, d\nu ,
\]

where \(c\) is the speed of light, \(\bar{\nu}\) the fundamental vibrational frequency in cm\(^{-1}\), \(n_1\) the index of refraction and \(e(\nu)\) the frequency dependent absorption coefficient in units of cm molecule\(^{-1}\) (base e). For electronic transitions Strickler and Berg [11] found that eq. (1) accurately predicted lifetimes to within 10%.

From our absorption spectrum of fig. 5 we estimate \(\int_{\text{band}} e(\nu) \, d\nu\) to be 1.2 \times 10\(^{-17}\) cm molecule\(^{-1}\), which is in good agreement with the value measured by Vu et al. [12] at a somewhat different temperature and pressure. Taking [13] \(n_1\) to be 1.23 eq. (1) yields \(k_{\text{CO}^{\ast},\text{rad}} = 65\ \text{s}^{-1}\). Considering that \(e(\nu)\) is known only to within 10\%, because that is the accuracy of our concentration measurement, and that there may be comparable error in the integration of \(e(\nu)\) the match between the calculated rate, 65 s\(^{-1}\), and the measure rate, 55 ± 2 s\(^{-1}\), seems reasonable.

The other method of calculating the liquid phase radiative relaxation rate is by correcting the gas phase rate for solution effects [13–15]. The liquid phase integrated absorption coefficient, can be related to the

![Fig. 4. Spectra of 0.0025 mole \% CO solution. The solid curve is total light collected from the undoped solution. Open dots represent a background spectrum taken with a doped sample such that fluorescence was quenched. The dashed line represents CO\(^{\ast}\) emission after the background is subtracted, and is normalized and replotted as \(S(\nu)\) in fig. 5.](image)

![Fig. 5. Absorbance and emission spectra of CO in liquid Ar. The emission spectrum is taken from fig. 4. The absorbance spectrum was taken with path length of 0.81 cm and CO concentration of 0.011 mole \%. Both spectra are used in our model for self-absorption, see text.](image)
The gas phase integrated absorption coefficient, by the relationship

\[ \int_{\text{band}} \epsilon(\nu) d\nu \approx \frac{1}{n_1} \left[ \frac{1}{2} (n_1^2 + 2) \right]^2 \int_{\text{band}} \epsilon(\nu) d\nu. \]  

(2)

The major assumption underlying eq. (2) is that a molecule dissolved in the liquid sees a different electric field due to the dielectric properties of the solvent. By combining eq. (1) and eq. (2) we obtain the relationship

\[ k_{CO^*,\text{rad}} \approx \frac{1}{2} n_1 (n_1^2 + 2)^2 \kappa_{\text{gas}}. \]  

(3)

By using eq. (3) we eliminate the need for measuring the integrated absorption coefficient which seems to be the major source of error in eq. (1), but we have a relationship which is extremely sensitive to \( n_1 \). Taking \[ \frac{\kappa_{\text{gas}}}{k_{CO^*,\text{rad}}} = 30 \text{ s}^{-1} \] eq. (3) yields \( k_{CO^*,\text{rad}} = 51 \text{ s}^{-1} \) which is in very good agreement with the measured \( 55 \pm 2 \text{ s}^{-1} \) rate.

It is also useful to compare the radiative rate in liquid Ar with that obtained for CO\(^*\) in liquid N\(_2\) of \( 51 \pm 5 \text{ s}^{-1} \). Taking the index of refraction of liquid nitrogen \( [11] \) to be \( n_1 = 1.20 \), the ratio of relaxation rates according to eq. (3) predicts the CO\(^*\) argon solution rate to be faster than the nitrogen solution rate by a factor of 1.07. The measured ratio is 1.09. The success of eq. (3) to estimate the lifetime of CO\(^*\) dissolved in liquid Ar and scale it for a different solution suggests that the dielectric properties of the solvent are the determining factor in the liquid phase radiative relaxation rate of CO\(^*\).

We measured the relaxation rate of CO\(^*\) in solid Ar at 80 K to be \( 66.8 \pm 2 \text{ s}^{-1} \). Dubost and Charneau [8] have studied CO\(^*\) fluorescence decay in Ar matrices between 10 and 30 K. For their purest samples, below 20 K, they obtain a rate of \( \approx 68 \text{ s}^{-1} \). However, above this temperature the relaxation rate decreases due to migration of CO\(^*\) to relaxing impurities. They interpret the limiting low temperature decay as radiative because diffusion of CO\(^*\) to interfering impurities which could open up radiationless channels is essentially halted. Since we see the same relaxation rate at 80 K as they saw below 20 K we conclude that our rate is solely radiative and not affected by impurities.

The increase in the CO\(^*\) radiative rate of 20% in the solid over that in the liquid solution is probably due to increases in integrated absorption coefficient and index of refraction. An increase of over 20% in the integrated absorption coefficient of CO has been observed when the liquid argon solution was solidified [12]. Unfortunately, the temperature and pressure conditions were so different from ours that a quantitative test of eq. (1) is not possible.

Above 0.01 mole % CO, the relaxation rate decreases because of self-absorption. This behavior has a simple explanation. As we have seen, the rate at which CO\(^*\) molecules radiate is given by \( k_{CO^*,\text{rad}} \). However, as the concentration of CO molecules increases they absorb a certain fraction, \( f \), of this radiation. Excitation may be re-emitted and reabsorbed a number of times, depending on concentration and cell geometry, before escaping to the detector. Because of this radiation trapping the system will have a slower, effective radiative rate we call \( k_{CO^*,\text{eff}} \). Radiation trapping effects were also observed in the liquid N\(_2\)–CO system and we developed [5] a model for the phenomena. Our model is similar to previous ones by Holstein [17] and Mitchell and Zemansky [18] and is based on two assumptions:

1. Light emitted and reabsorbed will be evenly redistributed throughout the sample and re-emitted.
2. The detection optics of the experiment collect a constant fraction of light from all parts of the volume that is interrogated. This volume is assumed to have a constant cross sectional area and a depth \( L \).

Using these two assumptions we have shown that

\[ k_{CO^*,\text{eff}} = f k_{CO^*,\text{rad}}. \]  

(4)

As the concentration of CO increases self-absorption causes \( k_{CO^*,\text{rad}} \) to decrease. The fraction of trapping is given by

\[ f = \frac{1}{L[CO]} \int_{\text{band}} \frac{S(\nu)}{\epsilon(\nu)} \left[ 1 - e^{-\epsilon(\nu)L[CO]} \right] d\nu. \]  

(5)

Here \( \epsilon(\nu) \) is the frequency dependent extinction coefficient taken from fig. 5 and \( L \) is the depth of the interrogated region. We pick \( L \) to be 0.5 cm for our apparatus because this represents approximately the shortest distance from the center of the cell to an exit window. We have taken the low concentration
emission data of fig. 4 (the dashed line) and normalized it according to
\[
\int_{\text{band}} S(\nu) \, d\nu = 1 .
\]

(6)

This emission profile, \( S(\nu) \), since it is obtained from the dilute solution is not influenced by self-absorption distortion. It appears in the upper part of fig. 5.

The results of the calculation expressed as \( \Gamma_{\text{obs}} = k_{\text{CO, rad}}^{(\text{ef})} \) are plotted as a dashed line in fig. 3. At the low concentration end, less than 0.01 mole \%, the rate is invariant with \( \text{CO} \) concentration. Here since the exponential in eq. (5) is small we have
\[
1 - \exp\left[-c(\nu) L [\text{CO}]\right] \approx c(\nu) L [\text{CO}]
\]
and term cancellations together with eq. (6) result in \( f = 1 \). We have then \( k_{\text{CO, rad}}^{(\text{ef})} = k_{\text{CO, rad}} \) throughout this region. At higher concentrations the exponential term vanishes and we find from eq. (5) that \( f \) decreases as \( [\text{CO}]^{-1} \).

The effective radiative rate is seen in fig. 3 to decrease inversely with \( \text{CO} \) concentration beyond 0.01 mole \%. There is good qualitative agreement of the data with the theoretical model up to a few mole \%. It is seen that radiative trapping has increased the lifetime of this system by over an order of magnitude. Above 3.0 mole \% CO the observed relaxation rate levels off and is considerably higher than the model would predict. Since the wings of the CO fluorescence profile are not well characterized by the low concentration data (see \( S(\nu) \) and \( c(\nu) \) of fig. 5) it seems reasonable that the model should not do well in predicting the lifetimes when emission escapes predominantly through the wings. Nevertheless as we shall show this leveling off in the observed rate provides us with a limit of an important radiationless relaxation channel for this system.

The observed relaxation rate for the CO—Ar solution is given by
\[
\Gamma_{\text{obs}} = k_{\text{CO, rad}}^{(\text{ef})} + k_{\text{CO, CO}}[\text{CO}]
\]
\[+ k_{\text{CO, Ar}}[\text{Ar}] + \sum_i k_{\text{CO, }X_i}[X_i] ,
\]

(7)

where \( k_{\text{CO, CO}} \) and \( k_{\text{CO, Ar}} \) represent \( V-T, R \) relaxation rate constants and \( k_{\text{CO, }X_i}[X_i] \) represents either a \( V-T, R \) or a \( V-V \) relaxation rate constant for excited CO colliding with an impurity \( X_i \).

We will now simplify eq. (7) and use our measured 100 mole \% concentration CO solution to place an upper limit on \( k_{\text{CO, CO}} \). For neat liquid carbon monoxide the third term in eq. (7) drops out. If we assume that the trends predicted by our model are present at high \( \text{CO} \) concentrations then \( k_{\text{CO, rad}}^{(\text{ef})} \) is not an important relaxation mechanism at 100 mole \% CO. Finally, by assuming that the impurities, \( X_i \), arise from introduction of the CO, they are therefore proportional to \([\text{CO}]\) with proportionality constant \( \alpha_{X_i} \) and eq. (7) reduces to
\[
\Gamma_{\text{obs}} = k_{\text{CO, CO}}[\text{CO}] + \sum_i \alpha_{X_i} k_{\text{CO, }X_i}[X_i] [\text{CO}]
\]
\[= 1.1 \pm 0.1 \text{ s}^{-1} .
\]

Using eq. (8) and taking \([\text{CO}] = 1.7 \times 10^{-22} \text{ molecule/cm}^3\) we obtain \( k_{\text{CO, CO}} \leq 6.5 \times 10^{-23} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1} \). This limit should first be compared with \( k_{\text{CO, CO}} \leq 5 \times 10^{-22} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1} \) obtained in our previous study of the \( \text{N}_2-\text{CO} \) system [5]. We believe the limits differ because another source of CO (Scientific Gas products “Research Grade”) was used to the \( \text{N}_2-\text{CO} \) experiments and the \( \sum_i \alpha_{X_i} k_{\text{CO, }X_i}[X_i] \) term contributed more to the observed relaxation rate. When this source of CO was used in the Ar—CO system the same, \( \leq 5 \times 10^{-22} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1} \), limit was obtained. Using the Airco “Research Grade” CO a lower upper limit for \( k_{\text{CO, CO}} \) was measured indicating a purer sample. The measured rate \( k_{\text{CO, CO}} \leq 6.5 \times 10^{-23} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1} \) compares well to the upper limit previously obtained of \( k_{\text{CO, N}_2} \leq 3 \times 10^{-23} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1} \). We would expect these two rates to be close due to similarities in the size, intermolecular potential and mass of CO and \( \text{N}_2 \).

Although there is no other experimental relaxation data to compare with our value of \( k_{\text{CO, CO}} \) Shin [19] has calculated the probability for CO relaxation by collision with CO as a function of temperature down to 100 K. Extrapolation of his curve to 85 K gives \( P_{\text{CO, CO}} = 5 \times 10^{-14} \). To compare our rate constant with this probability we will use the isolated binary collision model [20] for reaction rates. The model predicts that the observed rate is the product of the collision frequency, \( Z \), and probability of a relaxation per collision,
\[
k_{\text{CO, CO}}[\text{CO}] = Z P_{\text{CO, CO}} .
\]

(9)
In order to calculate $Z$ we use Madigosky and Litovitz's [21] cell model with moving walls,
\begin{equation}
Z = \bar{v}/([\text{CO}]^{-1/3} - a_{\text{CO}}),
\end{equation}
where $\bar{v}$ is the average thermal velocity, $[\text{CO}]$ the liquid density ($1.7 \times 10^{22}$ molecules/cm$^3$) and $a_{\text{CO}}$ the hard sphere diameter [22] of CO, $3.58 \times 10^{-8}$ cm. Using eqs. (9) and (10) and our upper limit for $k_{\text{CO}, CO}$ we calculate a probability of $9 \times 10^{-14}$. This may be fortuitously good agreement.

One of the objectives of this research, as stated in section 1, is to check liquid phase relaxation rate theories. Recently, Shin [23] calculated the vibrational relaxation of CO trapped in an Ar cell. The atoms comprising the cell are free to vibrate about their equilibrium positions. The vibrational energy of the CO* was then transferred to oscillatory states of the host atoms. At 85 K Shin predicted a relaxation rate of \approx 1000 s$^{-1}$. Our 3.0 mole % CO solution should satisfy the conditions of Shin's model with CO surrounded essentially by Ar atoms, but the measured relaxation rate is 1.8 s$^{-1}$. We therefore conclude that this model is not a realistic representation of Ar in the liquid phase.

Now that we have characterized the Ar-CO system we have begun to study vibrational relaxation of the systems CO-M in liquid argon where M = O$_2$, H$_2$, D$_2$, CH$_4$ and CF$_4$. These systems are particularly important because Simpson and co-workers [24-27] have recently published low temperature gas phase results for the systems CO-M, allowing us an excellent chance to make critical tests of the IBC model as it applies to vibrational relaxation in cryogenic liquids.

4. Conclusions

The conclusions of this paper can be summarized by the following five statements:

(1) Carbon monoxide dissolved in liquid Ar has a spontaneous emission rate of $55 \pm 2$ s$^{-1}$.

(2) Self-absorption decreases the relaxation rate as the concentration of CO increases up to \approx 3.0 mole % CO in a qualitatively predictable manner.

(3) By changing the concentration of CO the lifetime of the CO-Ar solution can be varied between 18 ms$^{-1}$ s$^{-1}$.

(4) The measured 100 mole % CO relaxation rate gives an upper limit on $k_{\text{CO}, CO}$ of $6.5 \times 10^{-23}$ cm$^3$ molecules$^{-1}$ s$^{-1}$.

(5) By monitoring the fluorescent emission from CO* in liquid Ar it is now possible to study the vibrational relaxation of carbon monoxide by a variety of molecules in order to test the IBC model.

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References
