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Temperature dependence of vibrational relaxation of N₂ by O₂ in liquid N₂ along the coexistence curve

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The temperature dependence of vibrational relaxation rates of N₂($\nu=1$) by O₂ in liquid N₂ has been studied at several temperatures along the coexistence curve between 80 and 120 K. A small amount of CO was added to the N₂-O₂ mixture as a pump and a probe. A CO laser was used to excite CO in solution and its fluorescence was monitored to obtain the rate of vibrational energy transfer. The liquid-phase rate constants k^l were compared with the gas-phase constants k^g at the same temperatures and found to be essentially equal. This result is in reasonable agreement with the predictions of the isolated binary collision model. © 1996 American Institute of Physics. [S0021-9606(96)02815-X]

I. INTRODUCTION

Vibrational energy may be stored in nitrogen more effectively than any other molecule. In the $\nu=1$ level, gaseous N₂ has a vibrational lifetime of ~ 5 s at room temperature and 1 atm pressure.¹ In the liquid state at 77 K, the lifetime increases to ~ 50 s. This lifetime is limited by IR radiation induced by its high density environment rather than collisional deactivation.^{2,3} Vibrationally excited nitrogen in the solid state similarly has lifetimes measured on the time scale of seconds.⁴ The ability of nitrogen to store vibrational energy in the gas phase is made use of in both the CO and CO₂ lasers.⁵ Nitrogen, however, has not yet been used as a liquid or solid state laser medium.

As part of our program to study liquid nitrogen as a medium for storing vibrational energy and to explore the effect of the liquid state on vibrational relaxation processes, energy transfer from N₂^{*} to O₂ in the liquid state has been monitored along the gas-liquid coexistence curve. (The asterisk is used to indicate the $\nu=1$ level of the molecule.)

In a previous study of this system the N₂ was vibrationally excited by stimulated Raman scattering and time dependence of N₂^{*} and O₂^{*} followed by spontaneous Raman scattering.⁶ Because the concentration of N₂^{*} was relatively high (~ 1 mole %) energy pooling occurred producing multiply excited O₂ which complicated the analysis of the kinetic data. Here we have doped liquid nitrogen with ¹³C¹⁶O and ¹³C¹⁸O isotopes which absorb radiation from a CO laser. Rapid energy exchange to N₂ then produces a low concentration of N₂^{*} which is then relaxed by O₂.

This paper progresses in the following order. After a description of experimental methods, the kinetics of the system are analyzed. Then the rate constants are extracted from the liquid state data and compared with gas phase results. The behavior of the rate constants in the liquid and in the gas phase is then compared with the prediction of an isolated binary collision (IBC) model of vibrational energy transfer.

II. EXPERIMENT

A schematic diagram of the experimental apparatus used is shown in Fig. 1. The light from a liquid N₂ cooled CO

laser, built in our laboratory after the design of Legay,⁷ was chopped mechanically and focused into a sample cell. Total power of up to 500 mW on all lines can be obtained with $\approx 10\%$ of which is for the $\nu=1 \rightarrow \nu=0$ transition at 2060 cm⁻¹. This transition overlaps well with the isotopically enriched CO absorption that occur at 2094 and 2042 cm⁻¹ for ¹³C¹⁶O and ¹³C¹⁸O, respectively. An interference filter was utilized to pass 2060–2160 cm⁻¹ radiation (the $\nu=1 \rightarrow \nu=0$ transition and some of the $\nu=2 \rightarrow \nu=1$ transition of the CO laser) into the cell. The light emitted from the excited CO in solution was collected at a right angle, and focused by an ellipsoidal mirror onto an InSb detector cooled to 77 K. An interference filter with a band pass between 2050–2150 cm⁻¹ was placed at the detector to reduce scattered light from the laser while passing most of the $1 \rightarrow 0$ radiation from the excited CO in the sample. The signal from the detector was amplified and fed into a Fabri-Tek model 1074 signal averager. Typically between 8 and 16 exponential decays were averaged and then sent to a chart recorder.

The brass sample cell, described elsewhere,⁸ was designed and built to withstand pressure up to 50 atm. At both the entrance and exit windows, LiF plugs were placed inside the cell to reduce laser light attenuation by the solution outside the probe region and to minimize self-absorption of the IR fluorescence. The cell was attached to the cold finger of a CSA-202 cryogenic refrigeration system made by Air Products. The temperature of the cell was stabilized to ± 2 K and read by a temperature controller model APD-D made also by Air products. The vapor pressure above the sample was used to calibrate the temperature measurements.

The sample was prepared by first introducing the desired amount of the gas mixture (CO and O₂) into the cell at room temperature, the cell was cooled to 77 K and then purified N₂ was condensed to form the liquid solution. The system was then isolated from the filling line to minimize the dead volume above the liquid and the change in liquid volume with temperature and vapor pressure. As the temperature was varied the concentration of O₂ between the liquid and gas phase changed. This concentration was determined by using solubility data^{9,10} and the temperature-density properties of liquid

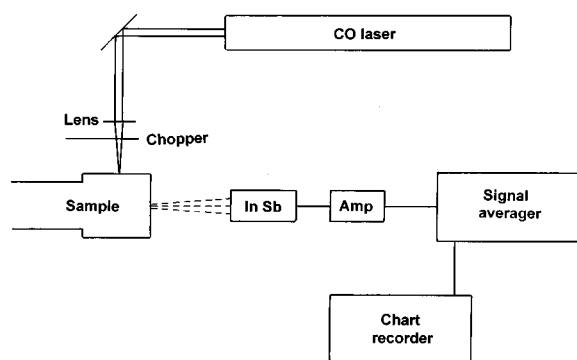


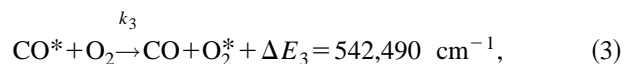
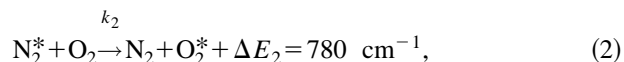
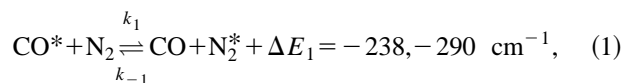
FIG. 1. Schematic diagram of the experimental apparatus.

nitrogen.¹¹ This procedure was checked by spectroscopic measurements on the dissolved CO. The concentrations are believed to be accurate to $\pm 10\%$.

The N₂ used was "Matheson Purity" from Matheson with stated minimum purity of 99.9995%. It was treated to remove traces of CO₂ and H₂O by passing it through a Linde type 4A molecular sieve cooled to dry ice temperature. Air Products "Research Grade" O₂ was used with a minimum purity of 99.996%. Carbon monoxide was obtained from Monsanto Research Corporation and had an isotopic composition of 88% ¹³C¹⁶O and 12% ¹³C¹⁸O. The gross composition was 99.12% CO, 0.12% CO₂, and 0.69% Ar together with the traces of other rare gases, and nitrogen. Both O₂ and CO were further purified by immersion of the cold fingers on gas storage bulb into liquid N₂ for several hours before mixture were prepared.

III. RESULTS AND DISCUSSION

Following excitation of CO to its $\nu=1$ vibrational level by the CO laser, the kinetics of the liquid mixture can be represented principally by the following equations:



Here, the vibrational levels of ¹³C¹⁶O*, ¹³C¹⁸O*, N₂*, and O₂* are located at 2094, 2042, 2332, and 1552 cm⁻¹, respectively.

Reaction (1), a near resonant process, has energy gaps $\Delta E_1 = -238 \text{ cm}^{-1}$ and $\Delta E_1 = -290 \text{ cm}^{-1}$ for the ¹³C¹⁶O and

¹³C¹⁸O isotopes, respectively. Reactions (2) and (3) are the V-V channels for relaxation of N₂* and CO*. The rate constant for reaction (2), k_2 , is what we have set out to measure. Reaction (4) involves relaxation of N₂* by trace impurity Y which we believe to be carbon dioxide carried to the system by carbon monoxide. Electric dipole IR radiation by CO* and collision-induced IR radiation by N₂* are described by reactions (5) and (6).

A number of relaxation channels have been neglected in the kinetic scheme we have just considered. For example, the reverse of reactions (2) and (3), were ignored since the Boltzmann factor requires $k_{-2} \sim 10^{-5} k_2$ and $k_{-3} \sim 10^{-4} k_3$. All V-T processes have been ignored.

The behavior of this system can be expressed analytically by

$$\begin{aligned} \frac{d[\text{CO}^*]}{dt} = & -(k_1[\text{N}_2] + k_3[\text{O}_2] + k_{\text{rad}}^{\text{CO}})[\text{CO}^*] \\ & + k_{-1}[\text{CO}][\text{N}_2^*], \end{aligned} \quad (7)$$

$$\begin{aligned} \frac{d[\text{N}_2^*]}{dt} = & k_1[\text{N}_2][\text{CO}^*] - (k_2[\text{O}_2] + k_{-1}[\text{CO}] - k_4[\text{Y}] \\ & + k_{\text{rad}}^{\text{N}_2})[\text{N}_2^*], \end{aligned} \quad (8)$$

$$\frac{d[\text{O}_2^*]}{dt} = k_3[\text{O}_2][\text{CO}^*] + k_2[\text{O}_2][\text{N}_2^*]. \quad (9)$$

The solution for the time dependent concentration of CO* from these coupled differential equations is¹²

$$\begin{aligned} [\text{CO}^*] = & A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t) \\ & + A_3 \exp(-\lambda_3 t), \end{aligned} \quad (10)$$

where A_1 , A_2 , and A_3 are constants and λ_1 , λ_2 , and λ_3 represent three different decay rates for CO*. Simpson *et al.*¹³ obtained an analytical expression for the slow part of the decay, which is of interest in this experiment, given by

$$\lambda_2 = \Gamma_{\text{obs}} = \frac{(k_3[\text{O}_2] + k_{\text{rad}}^{\text{CO}})B^2 + k_2[\text{O}_2]A^2}{A^2 + B^2} + k_{\text{rad}}^{\text{N}_2} + k_4[\text{Y}], \quad (11)$$

where, $A = k_1[\text{N}_2]$ and $B = k_{-1}[\text{CO}]$.

Reaction (1) occurs most rapidly, with measured¹⁴ gas phase rate constant $k_1 = 1.1 \times 10^{-17} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ at 77 K for the ¹³C¹⁶O isotope. Under our experimental conditions, $[\text{N}_2]/[\text{CO}] \sim 10^4$, and since the Boltzmann factor requires $k_{-1}/k_1 \sim 10^1 - 10^2$ (depending on the temperature), then A is 2-3 orders of magnitude larger than B , and $A^2 + B^2 \approx A^2$. Measured^{13,14} gas phase rate constants for processes in Eqs. (2) and (3) shows that k_3 is an order of magnitude greater than k_2 . The radiative rate constant $k_{\text{rad}}^{\text{CO}}$, measured¹⁵ in our laboratory, has a value of $\sim 40 \text{ s}^{-1}$. Therefore, $(k_3[\text{O}_2] + k_{\text{rad}}^{\text{CO}})B^2$ is 3-5 orders of magnitude smaller than $k_2[\text{O}_2]A^2$. Taking the relative magnitudes of terms in Eq. (11) into consideration, the equation can be simplified to the form

$$\Gamma_{\text{obs}} \approx k_2[\text{O}_2] + k_{\text{rad}}^{\text{N}_2} + k_4[\text{Y}]. \quad (12)$$

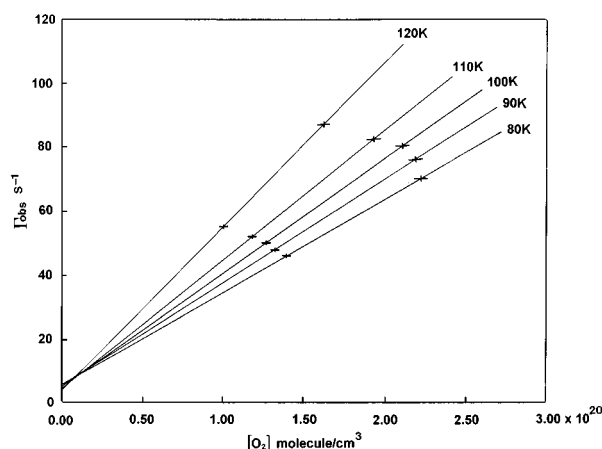


FIG. 2. Rate of relaxation of CO* in liquid nitrogen–oxygen solutions. $[CO]/[N_2]=2.3 \times 10^{-4}$ for all experiments.

Equation (12) shows that, for small concentrations of CO, the observed rate depends predominantly on the concentration of O₂. A plot of Γ_{obs} vs $[O_2]$ should give a straight line with slope equals to k_2 .

The relaxation rate for N₂/CO solutions with $[O_2]=0$ is $\Gamma_{\text{obs}}=4.0 \text{ s}^{-1}$ at 120 K and increasing slightly with decreasing temperature to become 5.4 s^{-1} at 80 K. The collision—induced radiation lifetime of N₂* at 77 K has been estimated, to be $k_{\text{rad}}^{\text{N}_2}=0.012 \text{ s}^{-1}$. Using $\Gamma_{\text{obs}} = k_{\text{rad}}^{\text{N}_2} + k_4[Y]$ for $[O_2]=0$ we conclude then that $k_4[Y] \sim 4\text{--}5.4 \text{ s}^{-1}$ throughout our temperature range. Carbon dioxide is present in our carbon monoxide to the extent of 1.2 part per thousand and because of the expense of the heavy isotope effective purification was not possible. At a concentration of 1 part per million in liquid nitrogen, CO₂ is known¹⁶ to increase the relaxation rate to 3 s^{-1} at 77 K. We believe this impurity to be responsible for the $[O_2]=0$ rates in our experiments. Since we obtain k_2 from the slopes of the rate curves these complications do not effect our results.

Relaxation of solutions of various concentration of $[O_2]$ and several temperatures are shown in Fig. 2. From the slopes of these curves and Eq. (12) we find $k_2=(2.9 \pm 0.3) \times 10^{-19} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ at 80 K gradually increasing to $(5.0 \pm 0.5) \times 10^{-19} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ at 120 K. We may compare these rate constants with low temperature gas phase measurements of Maricq *et al.*¹⁴ as shown in Table I. Unfortunately, because relaxation in the gas phase at low temperatures is so inefficient the precision error in the rate constants is often as great as 30%. Within the limits of experimental error the gas-phase and liquid-phase rate constants are essentially the same over this temperature range.

We note that these liquid state rate constants are significantly larger than those reported by Calaway and Ewing.⁶ At 77 K they reported $k_2=1.2 \times 10^{-19} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ which is less than half the value we obtained near this temperature. In the previous study using stimulated Raman scattering, the laser focusing required to produce vibrational excitation yielded $[N_2^*]/[N_2] \sim 1\%$ which was comparable to the mole fraction of oxygen of $[O_2]/[N_2] \sim 1\%$. Thus transfer

TABLE I. Vibrational relaxation of N₂* by O₂ in the liquid phase and the gas phase.

| T | k^{la} | k^{gb} | $k^{\text{l}}/k^{\text{g}}$ ^c |
|-----|-----------------------|-----------------------|--|
| 80 | 2.9×10^{-19} | | |
| 90 | 3.3×10^{-19} | 2.2×10^{-19} | 1.6 ± 0.5 |
| 100 | 3.6×10^{-19} | 2.7×10^{-19} | 1.4 ± 0.4 |
| 110 | 4.0×10^{-19} | 3.3×10^{-19} | 1.3 ± 0.4 |
| 120 | 5.0×10^{-19} | 4.0×10^{-19} | 1.3 ± 0.4 |

^aThis work.

^bFrom Ref. 14.

^cA 10% error in the liquid phase and a 20% error in the gas phase have been used in obtaining this ratio.

of energy from N₂* to O₂ would initially produce $[O_2^*]/[O_2] \sim 100\%$ which would be expected to be followed by energy pooling to produce O₂($v=2$), O₂($v=3$), etc. through Treaner–Teare pumping.¹⁷ The previously observed non-linear Γ_{obs} vs $[O_2]$ curve is consistent with energy pooling and the deconvolution of the relaxation measurements to yield accurate value of k_2 was obviously unsuccessful. In the present experiments the cw CO laser delivered $\sim 1 \text{ W}$ ($\sim 2 \times 10^{19}$ photons s^{-1}) of which 10% was absorbed. During the effective lifetime of the system, 10^{-1} s , 2×10^{17} vibrational quanta (i.e., N₂*) were produced in a sample volume of 0.25 cm^3 yielding $[N_2^*] \sim 8 \times 10^{17} \text{ molecule cm}^{-3}$. The fraction of excited nitrogen molecules is thus $[N_2^*]/[N_2] \sim 5 \times 10^{-5}$ or much less than the acceptor fraction of $[O_2]/[N_2] \sim 1 \times 10^{-2}$. Energy pooling in our experiments is thus unlikely. Indeed we looked for changes in the relaxation rates by varying laser fluence but found none.

Vibrational relaxation of CO* by O₂ was studied in the gas,¹³ liquid,⁸ and the solid¹⁸ phase in a rare-gas matrices, at various temperatures. The V–V rate constants obtained are an order of magnitude larger than that for N₂–O₂. This is due mainly to the smaller energy gap between CO($v=1$) and O₂($v=1$) levels, $\Delta E=587 \text{ cm}^{-1}$, compared to $\Delta E=780 \text{ cm}^{-1}$ between N₂($v=1$) and O₂($v=1$) levels.

Simpson *et al.*^{19,20} measured the rate constants for the vibrational deactivation of the isotopes of CO by the collision partners, O₂, CH₄, CH₃D, CD₃H, and CD₄ both in liquid Kr solution at 118 K and in liquid Ar at 85 K, and in the gas phase at the same temperatures. The ratio of the rate constants, $k^{\text{l}}/k^{\text{g}}$, obtained is 1.03 in liquid Ar (Ref. 19) and 1.39 in liquid Kr (Ref. 20). Within the experimental errors this is in agreement with our $k^{\text{l}}/k^{\text{g}}$ ratio.

The isolated binary collision model²¹ provides a method to evaluate the influence of the liquid environment on the vibrational relaxation rate constant. It maintains that only binary collisions are responsible for the relaxation process. Consequently, the rate constant is scaled by the probability that the colliding molecules are at an effective distance, r_{ef} , for the relaxation to occur. This probability is obtained from the pair distribution function $g(r_{\text{ef}}, T, \rho)$ and depends on effective molecular separation r_{ef} , the temperature T , and fluid density ρ . The result of the IBC model is to express the ratio of the liquid state and gas phase rate constants as a ratio of the corresponding pair distribution functions:

$$\frac{k^l}{k^g} = \frac{g^l(r_{\text{ef}}, T, \rho)}{g^g(r_{\text{ef}}, T, \rho)}. \quad (13)$$

For the dilute gas, ($\rho \rightarrow 0$), the pair distribution function is simply $g^g(r_{\text{ef}}, T, \rho) = \exp[-V(r_{\text{ef}})/kT]$, where $V(r_{\text{ef}})$ is the intermolecular potential function, e.g., the Lennard-Jones 6-12 evaluated at r_{ef} . Determination of $g^l(r_{\text{ef}}, T, \rho)$ is more involved and requires a molecular dynamics calculation or other treatment of the dense fluid state. Such evaluations are available²² but principally for neat, monatomic fluids governed by an isotropic Lennard-Jones potential. Our system is a ternary solution and efficient relaxation is expected to occur at close ($r_{\text{ef}} = 0.90\sigma$ to 0.95σ) collision where anisotropic effects are expected to be important. Another difficulty is the determination of r_{ef} . A simple model^{14,15} can be used to calculate r_{ef} from k^g for collisions of N₂^{*}+O₂ over an isotropic Morse Potential. Using $D_e = 115$ K and $a = 2.1 \times 10^8$ cm⁻¹ for the intermolecular potential well depth²³ and range parameter,¹⁴ give $k^g = 2 \times 10^{-19}$ molecule⁻¹ cm³ s⁻¹ at 90 K and 5×10^{-19} molecule⁻¹ cm³ s⁻¹ at 120 K consistent with the experimental results. Examination of these theoretical results shows that the most effective collisions at 90 K have an energy of $E_{\text{ef}} = 440$ K and those most effective at 120 K are at $E_{\text{ef}} = 570$ K. The energy of the effective collisions are thus almost five times kT . These results are a consequence of a compromise between an *increase* of probability of relaxation with energy of collision but a *decrease* in the Boltzmann population of collisions with high energy. The corresponding effective distance at these temperatures (obtained from $V(r_{\text{ef}}) = E_{\text{ef}}$) is 0.93σ at 90 K and 0.90σ at 120 K. Corresponding values of $g^l(r_{\text{ef}}, T, \rho)/g^g(r_{\text{ef}}, T, 0)$ are ~ 2 for $T = 90$ K and ~ 3 at 120 K using Verlet's tables²² or perturbation recipes given by Chesnoy²⁴ who has adapted the results of the WCA model describing liquids.²⁵ These ratios seem significantly larger than the ratios of k^l/k^g in Table I. Had we used $r_{\text{ef}} = \sigma$ the results for the ratio of the pair distribution functions would have been 1.2 and 1.1 at 90 K and 120 K, which is equal to k^l/k^g values in Table I. Within the web of assumptions needed to evaluate $g^l(r_{\text{ef}}, T, \rho)/g^g(r_{\text{ef}}, T, 0)$ we cannot attach any significance to the apparent discrepancy between the measured and predicted ratio k^l/k^g .

In conclusion, we feel that the IBC model is thus a useful *guide* to understanding k^l/k^g but realistic quantitative applications are difficult to achieve.

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