

The influence of the attractive well on near-resonant vibrational energy transfer in the gas phase: the importance of third body collisions

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Abstract

In a recent paper we postulated that for both non-resonant and near-resonant (VV) energy transfer orbiting collisions become important at temperatures below the Lennard-Jones well depth. We show here that the rate constants for near-resonant (VV) processes are affected by the third body collision partners H_2 , He and Ne, which stabilise the collision complex and reduce the probability for energy transfer. The reverse behaviour has been found for argon which may form dimers with the excited molecules, increasing the collision cross-section. © 1997 Elsevier Science B.V.

1. Introduction

Recently we have investigated the influence of the attractive well on near- and non-resonant vibrational energy transfer in the gas phase [1]. Rate constants were measured for the (VV) transfers between $CO(v=1)$ and the deuterioisomers of methane over the temperature range 55–200 K. Transfer between $^{13}C^{18}O(v=1)$ and CH_4 is non-resonant whilst the transfers between $^{12}C^{16}O(v=1)$ and CD_3H and between $^{12}C^{16}O(v=1)$ and CD_4 are close to resonance. At temperatures below the Lennard-Jones well depth of 120 K for the CO–methane dimer [2], the temperature dependences of the rate constants for the two classes of system are strikingly different. For the non-resonant transfer from $^{13}C^{18}O(v=1)$ to CH_4 , the positive temperature dependence of the rate constants flattens below 85 K. This is reminiscent of the upturn in rate constants observed for the deactivation of $CO(v=1)$ by H_2 , HD and D_2 which occurs just

below the well depth of 64 K [3,4]. In contrast, the rate constants for the near-resonant transfers to CD_3H and CD_4 fall dramatically with decrease in temperature below 85 K. This is in complete disagreement with the qualitative predictions of semi-classical theories of near-resonant (VV) energy transfer [5–7] which predict that the rate constants should increase with decrease in temperature, a behaviour which is observed for these systems at temperatures above 85 K.

A similar contrasting behaviour has been seen in the (VV) transfer rate constants between $^{12}C^{16}O(v=1)$ and $^{13}C^{16}O(v=0)$ and between $^{12}C^{16}O(v=1)$ and $^{13}C^{18}O(v=0)$ [8]. The rate constants for the $^{12}C^{16}O$ – $^{13}C^{18}O$ system, which of the two systems is furthest in energy from a resonant condition with an energy mismatch of 100 cm^{-1} , decrease with decrease in temperature in the range 270–80 K and then flatten and increase with decrease in temperature below 80 K. For the system $^{12}C^{16}O$ – $^{13}C^{16}O$,

which is closer to resonance with an energy mismatch of 47 cm^{-1} , the rate constants increase with decrease in temperature in the range 270–80 K whilst below 80 K they flatten and then turn down. The Lennard-Jones well depth for these systems is 100 K (69 cm^{-1}) [2]. Downturns in rate constants have also been observed for the near-resonant (VV) transfers between $^{12}\text{C}^{16}\text{O}$ and $^{14}\text{N}_2\text{O}$ and for $^{12}\text{C}^{16}\text{O}$ and $^{15}\text{N}_2\text{O}$ [9].

We have postulated that for both non- and near-resonant vibrational energy transfer, orbiting collisions occur at temperatures at which the attractive well influences the collisional process. The orbiting collisions can be stabilised by third body collisions to form a van der Waals dimer if their duration is sufficiently long [1,8]. For processes which have an energy mismatch larger than the well depth, such as non-resonant (VV) and (VT) energy transfer, after the energy has been released the collision partners may readily escape the attractive well and separate. The orbiting collision enhances the probability of energy transfer as multiple collisions can occur during the increased time in which the collision pair are in close proximity. An example of a process which is sufficiently exothermic for the collision pair to escape from a stabilised complex is the (VV) transfer from $^{12}\text{C}^{16}\text{O}(v=1)$ to $^{13}\text{C}^{18}\text{O}(v=1)$, which is exothermic by 100 cm^{-1} with the CO–CO well depth being only 69 cm^{-1} . However, for (VV) processes close to resonance, insufficient energy may be released for the collision pair to escape the well. In transfer from $^{12}\text{C}^{16}\text{O}(v=1)$ to $^{13}\text{C}^{16}\text{O}(v=1)$, the energy mismatch is 47 cm^{-1} and the well depth is 69 cm^{-1} : the process is insufficiently exothermic to guarantee escape from the well following energy transfer. The stabilisation of the complex suppresses the (VV) transfer and escape from the well in favour of a less efficient, more exothermic, pathway.

The results of these studies of (VV) energy transfer at low temperatures suggest that third body collisions are important [1,8]. If the mechanism discussed above is correct, the rate constants for the near-resonant (VV) transfer processes should be dependent on the nature and pressure of the buffer gas used. A systematic study of the dependence of rate constants for the near-resonant CO–CD₃H system on the buffer gas has been undertaken and the results are presented here. The CO–CD₃H system is a suitable system for

the study of third body effects. Unlike the CO–CO systems [8], the (VV) transfer can be rendered irreversible by adding hydrogen to the experimental gas phase mixture. This rapidly deactivates the CD₃H, with a vibrational energy of 2142 cm^{-1} , to vibrational states about 1000 cm^{-1} lower in energy, but does not deactivate CO($v=1$) on a comparably short time-scale since all of its 2143 cm^{-1} vibrational quantum must be relaxed by a single collision [10–12]. A similar strategy cannot be adopted for the CO–CO studies and the fluorescence from one of the CO species must be filtered out with the system being investigated under reversible conditions. The CO–CD₃H system is also suitable for study in that it is only 1 cm^{-1} from exact resonance and thus the semi-classical theories of near-resonant (VV) energy transfer mediated by long-range forces would be expected to be most applicable [5–7]. Rate constants have been measured for the four buffer gases hydrogen, helium, neon and argon over a range of pressures and temperatures at temperatures below that at which the influence of the attractive well becomes apparent.

2. Experimental

The laser excited infrared fluorescence technique was used for the present study. The apparatus has been described in detail in previous publications [3,13] and only a brief description will be given here. Excitation of $^{12}\text{C}^{16}\text{O}$ from its ground state to its first vibrationally excited state is achieved by using a frequency doubled CO₂ laser. The laser is operated on the 9R(18) regular band transition, which, when frequency doubled, lies within 0.007 cm^{-1} of the R(2) line of $^{12}\text{C}^{16}\text{O}$. Frequency doubling is achieved by means of an AgGaSe₂ crystal with the laser power of the fundamental radiation attenuated, prior to reaching the doubling crystal, by two ZnSe windows mounted at the Brewster angle. Pulse energies of the frequency doubled radiation are in the range 0.5 to 1 mJ.

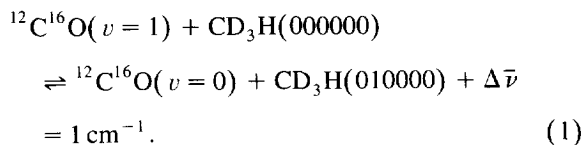
Experiments are performed in a fluorescence cell, housed inside a modified Oxford Instruments cryostat. The cell may be cooled with either liquid N₂ or liquid He and the temperature of the cell can be stabilised to within $\pm 0.1\text{ K}$ for prolonged periods of

time. A liquid N₂ cooled InSb detector is mounted in the perpendicular vertical plane to the incident frequency doubled radiation. Fluorescence traces are collected by a Datalab DL912 transient recorder and analysed by custom written software.

Gas mixtures are prepared in a gas handling line which has a typical base pressure of 1×10^{-5} Torr. All mixtures are cooled with dry ice prior to an experiment in order to remove traces of condensable impurities, especially water vapour, which may give anomalous results. The purities of the gases used have been given in our previous publication [1]. In addition: the purity of argon is 99.9999% with principal impurities (O₂ < 1, N₂ < 1, CO₂ < 1, hydrocarbons < 1, H₂O < 1) ppm, the purity of helium is 99.998% with principal impurities (N₂ 10, Ne 5, O₂ 2, Ar < 1, H₂ 1, CO₂ < 1, hydrocarbons < 1, H₂O < 2) ppm, and the purity of hydrogen is 99.9997% with principal impurities (N₂ < 1, O₂ < 1, CO₂ < 0.05, CO < 1, hydrocarbons < 1, H₂O < 1) ppm. At the temperatures of these experiments of less than 100 K, trace impurities of H₂O, CO₂ and heavy hydrocarbons will be frozen out on the cell walls.

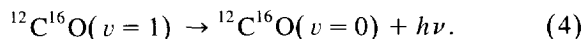
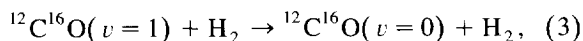
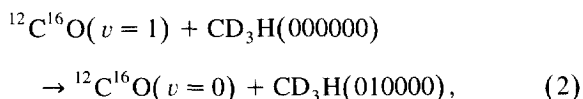
3. System analysis

Of all the near-resonant and non-resonant systems studied in our previous publications [1,14,15], the influence of third body collisions has been investigated for the one which is closest to resonance: the CO–CD₃H system. The dominant near-resonant transition is from the first vibrationally excited state of CO to the ν_2 C–D stretching vibration of CD₃H and this is only 1 cm^{-1} from exact resonance [16].



If the coupling is to this single level of CD₃H of known degeneracy, the forward and backward rate constants for process (1) are related by the principle of microscopic reversibility. If the transfer is measured under reversible conditions, all of the processes which deactivate the CO–CD₃H coupled pair

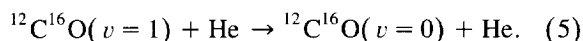
must be included in the kinetic analysis. The processes which must be considered include the coupling of the ν_2 vibration of CD₃H with the other vibrational modes of CD₃H around 2000 cm^{-1} , with their particular degeneracies. Rate constants for these processes are not known. This problem can be overcome and the rate constants for process (1) measured accurately if the transfer is rendered irreversible. This is achieved by adding hydrogen to the gas mixture which is an efficient relaxant of CD₃H(010000) for which the rate constant at 100 K for relaxing the CD₃H ν_2 mode is about 10,000 times greater than that for the relaxation of CO($v=1$) [1,3,12]. The CD₃H(010000) is rapidly coupled by H₂ to the levels at around 1000 cm^{-1} lower in energy with rotational excitation of the H₂ and consequently only one excited species, CO($v=1$), need be considered in the kinetic analysis. This is applicable only if the CD₃H–H₂ coupling rate is made to be much faster than the backward transfer of energy from CD₃H to CO: in the work presented here the relaxation rate of CD₃H(010000) by H₂ is typically between 100 and 1000 times faster than the backward (VV) transfer. That the (VV) transfer is measured under irreversible conditions has been checked by varying the amount of H₂ present in the gas mixture by a factor of 10 for different experiments [1]. Only three steps must then be considered in the kinetic analysis, with the rate of deactivation of the excited species, CO($v=1$), by impurities in the gas sample being negligible,



Rate constants for process (2) have been measured in the present study down to a temperature of 70 K. To measure rate constants at such a low temperature, it is necessary to ensure that the condensation of CD₃H or adsorption onto the cell walls is avoided. The kinetic analysis is dependent on knowing accurately the partial pressure of CD₃H. In all of the experiments presented here, the partial pressure of CD₃H was more than an order of magni-

tude less than its vapour pressure at the temperature of measurement [17]. The reproducibility of the results with different gas mixture compositions also attests to the validity of the analysis.

To investigate the influence of third body collisions on process (2), rate constants have been measured in gas mixtures buffered by pure H_2 and mixtures containing a fixed partial pressure of H_2 with the addition of the buffer gases He, Ne and Ar. Although the rate of deactivation of $\text{CO}(v=1)$ by the Ne or Ar buffer is negligible at the pressures employed [7], the rate of deactivation of $\text{CO}(v=1)$ by He is significant and one further process must be included in the kinetic scheme.



The rate constants for this process are known accurately [3]. Finally, the partial pressure of hydrogen was maintained at approximately the same level in all of the experiments presented here in order that the contribution to third body effects from H_2 is constant. The partial pressure of H_2 used, 20 Torr, was the same as that used in our earlier study for which the transfer is known to be irreversible [1].

4. Results

Rate constants have been measured for the deactivation of $^{12}\text{C}^{16}\text{O}(v=1)$ by CD_3H in a pure H_2 buffer at 100 Torr. The variation of the rate constants with hydrogen at pressures above 100 Torr cannot be investigated as process (2) and the deactivation of $^{12}\text{C}^{16}\text{O}(v=1)$ by H_2 would have comparable rates, while at pressures below 80 Torr the rate of diffusion of the excited species out of the field of view of the detector is significant and the measured rate of relaxation of $^{12}\text{C}^{16}\text{O}(v=1)$ is artificially increased. The results of the hydrogen buffering experiments are given in Table 1 and in Fig. 1.

In experiments with helium as a buffer gas, the helium gas pressure has been varied between 93 and 475 Torr. The rate constants for the (VV) transfer are given in Table 2 and in Fig. 1. Buffer pressures in the range 106–477 Torr have been used to investigate third body effects in a neon buffer and the rate constants are given in Table 3. In both buffer gases the rate constants fall dramatically below 85 K.

Table 1

The dependence of the rate constants for the vibrational deactivation of $^{12}\text{C}^{16}\text{O}(v=1)$ by CD_3H on the buffer gas: hydrogen buffer gas

Temperature / K	$k_{^{12}\text{C}^{16}\text{O}-\text{CD}_3\text{H}} / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
120	$(8.3 \pm 0.9)(-13)^a$
100	$(1.15 \pm 0.05)(-12)^a$ $(1.16 \pm 0.03)(-12)^b$
90	$(1.23 \pm 0.04)(-12)^a$ $(1.22 \pm 0.04)(-12)^b$
80	$(1.05 \pm 0.03)(-12)^a$ $(1.01 \pm 0.03)(-12)^b$
71	$(6.8 \pm 0.3)(-13)^b$
70	$(6.1 \pm 0.4)(-13)^a$

Compositions by mole fraction:

^a $7.49 \times 10^{-5} \text{ CD}_3\text{H}$, $7.55 \times 10^{-5} ^{12}\text{C}^{16}\text{O}$, balance H_2 . Pressure 103 Torr.

^b $7.49 \times 10^{-5} \text{ CD}_3\text{H}$, $1.00 \times 10^{-4} ^{12}\text{C}^{16}\text{O}$, balance H_2 . Pressure 100 Torr.

Note: $(A \pm B)(-C) = (A \pm B) \times 10^{-C}$.

Rate constants in an argon buffer gas can only be measured at a pressure of around 100 Torr below 85 K. Larger pressures of argon are too close to its vapour pressure and condensation occurs, whilst at lower pressures the buffer gas pressure is not sufficient to prevent the diffusion of the excited species out of the field of view of the detector. Rate con-

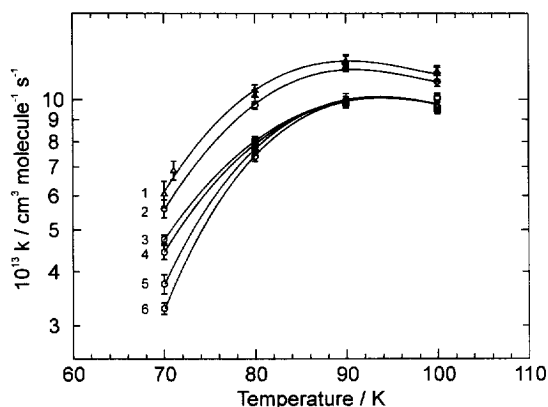


Fig. 1. The dependence of the rate constants for the vibrational deactivation of $^{12}\text{C}^{16}\text{O}(v=1)$ by CD_3H on the buffer gas pressure: H_2 and He buffer gases. (1) H_2 at 100 Torr. (2) He at 93 Torr and H_2 at 20 Torr. (3) He at 105 Torr and H_2 at 20 Torr. (4) He at 201 Torr and H_2 at 20 Torr. (5) He at 475 Torr and H_2 at 20 Torr. (6) He at 480 Torr and H_2 at 20 Torr.

Table 2

The dependence of the rate constants for the vibrational deactivation of $^{12}\text{C}^{16}\text{O}(v=1)$ by CD_3H on the buffer gas for mixture containing 20 Torr of H_2 and various pressures of helium

p_{He} / Torr	$k_{^{12}\text{C}^{16}\text{O}-\text{CD}_3\text{H}} / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$			
	$T = 100$	$T = 90$	$T = 80$	$T = 70$
93	$(1.10 \pm 0.03)(-12)^a$	$(1.18 \pm 0.02)(-12)^a$	$(9.7 \pm 0.2)(-13)^a$	$(5.6 \pm 0.2)(-13)^a$
105	$(9.6 \pm 0.2)(-13)^b$	$(1.00 \pm 0.02)(-12)^b$	$(8.0 \pm 0.2)(-13)^b$	$(4.8 \pm 0.1)(-13)^b$
	$(9.6 \pm 0.3)(-13)^c$	$(1.00 \pm 0.04)(-12)^c$	$(7.9 \pm 0.2)(-13)^c$	
201	$(9.4 \pm 0.2)(-13)^d$	$(9.8 \pm 0.2)(-13)^d$	$(8.08 \pm 0.04)(-13)^d$	$(4.4 \pm 0.2)(-13)^d$
475	$(1.01 \pm 0.02)(-12)^e$	$(9.7 \pm 0.1)(-13)^e$	$(7.4 \pm 0.2)(-13)^e$	$(3.7 \pm 0.2)(-13)^e$
480	$(1.01 \pm 0.02)(-12)^f$	$(9.8 \pm 0.2)(-13)^f$	$(7.6 \pm 0.2)(-13)^f$	$(3.3 \pm 0.1)(-13)^f$

Compositions by mole fraction:

^a 6.71×10^{-5} CD_3H , 6.75×10^{-5} $^{12}\text{C}^{16}\text{O}$, 1.67×10^{-1} H_2 , balance He. Pressure 114 Torr.

^b 4.02×10^{-5} CD_3H , 5.93×10^{-5} $^{12}\text{C}^{16}\text{O}$, 1.48×10^{-1} H_2 , balance He. Pressure 125 Torr.

^c 3.99×10^{-5} CD_3H , 4.00×10^{-5} $^{12}\text{C}^{16}\text{O}$, 1.48×10^{-1} H_2 , balance He. Pressure 126 Torr.

^d 3.34×10^{-5} CD_3H , 3.38×10^{-5} $^{12}\text{C}^{16}\text{O}$, 9.11×10^{-2} H_2 , balance He. Pressure 222 Torr.

^e 1.52×10^{-5} CD_3H , 1.54×10^{-5} $^{12}\text{C}^{16}\text{O}$, 3.74×10^{-2} H_2 , balance He. Pressure 493 Torr.

^f 1.03×10^{-5} CD_3H , 1.48×10^{-5} $^{12}\text{C}^{16}\text{O}$, 3.75×10^{-2} H_2 , balance He. Pressure 499 Torr.

Note: $(A \pm B)(-C) = (A \pm B) \times 10^{-C}$.

stants are presented in Table 4. The temperature dependence of the rate constants remains negative down to a temperature of 75 K and this is in good agreement with the earlier study of Allen et al. [14].

The rate constants have been measured in neon-argon buffer gas mixtures and the results are presented in Table 5 and in Fig. 2. The dependence of the rate constants on the partial pressure of argon is weak. Even with only 5 Torr of argon in the mixture and 101 Torr of neon, the rate constants for the (VV) transfer fall midway between those measured in pure

neon and those in pure argon at a similar total pressure. A comparison of the rate constants measured in two buffer mixtures which contain almost the same partial pressure of neon, 107 Torr and 108 Torr, but different pressures of argon, 6 Torr and 0 Torr respectively, is instructive. It suggests that it is not only neon which is having an effect in reducing the likelihood of the (VV) process on collision, but that argon is having the converse effect and increases the likelihood of (VV) transfer on collision of $^{12}\text{C}^{16}\text{O}$ with CD_3H . This result is confirmed by the

Table 3

The dependence of the rate constants for the vibrational deactivation of $^{12}\text{C}^{16}\text{O}(v=1)$ by CD_3H on the buffer gas for mixture containing 20 Torr of H_2 and various pressures of neon

p_{Ne} / Torr	$k_{^{12}\text{C}^{16}\text{O}-\text{CD}_3\text{H}} / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$				
	$T = 100$	$T = 90$	$T = 80$	$T = 75$	$T = 70$
106	$(9.6 \pm 0.3)(-13)^a$	$(9.4 \pm 0.2)(-13)^a$	$(6.7 \pm 0.2)(-13)^a$	$(4.9 \pm 0.3)(-13)^a$	$(3.6 \pm 0.1)(-13)^a$
110	$(9.1 \pm 0.2)(-13)^b$	$(9.0 \pm 0.2)(-13)^b$	$(6.8 \pm 0.1)(-13)^b$	$(5.2 \pm 0.1)(-13)^b$	$(3.9 \pm 0.1)(-13)^b$
282	$(9.4 \pm 0.2)(-13)^c$	$(9.1 \pm 0.1)(-13)^c$	$(6.8 \pm 0.2)(-13)^c$	$(5.0 \pm 0.1)(-13)^c$	$(3.7 \pm 0.1)(-13)^c$
477	$(1.0 \pm 0.02)(-12)^d$	$(9.9 \pm 0.2)(-13)^d$	$(7.6 \pm 0.1)(-13)^d$	$(5.1 \pm 0.2)(-13)^d$	$(3.6 \pm 0.1)(-13)^d$

Compositions by mole fraction:

^a 5.91×10^{-5} CD_3H , 6.03×10^{-5} $^{12}\text{C}^{16}\text{O}$, 1.48×10^{-1} H_2 , balance Ne. Pressure 124 Torr.

^b 5.81×10^{-5} CD_3H , 7.56×10^{-5} $^{12}\text{C}^{16}\text{O}$, 1.43×10^{-1} H_2 , balance Ne. Pressure 128 Torr.

^c 2.38×10^{-5} CD_3H , 3.12×10^{-5} $^{12}\text{C}^{16}\text{O}$, 5.90×10^{-2} H_2 , balance Ne. Pressure 300 Torr.

^d 1.52×10^{-5} CD_3H , 1.97×10^{-5} $^{12}\text{C}^{16}\text{O}$, 3.72×10^{-2} H_2 , balance Ne. Pressure 495 Torr.

Note: $(A \pm B)(-C) = (A \pm B) \times 10^{-C}$.

Table 4

The dependence of the rate constants for the vibrational deactivation of $^{12}\text{C}^{16}\text{O}(v=1)$ by CD_3H on the buffer gas for mixture containing 20 Torr of H_2 and various pressures of argon

Temperature /K	$k_{^{12}\text{C}^{16}\text{O}-\text{CD}_3\text{H}} / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
100	$(1.12 \pm 0.02)(-12)^a$ $(1.09 \pm 0.02)(-12)^b$
90	$(1.36 \pm 0.02)(-12)^a$ $(1.20 \pm 0.03)(-12)^b$
85	$(1.42 \pm 0.07)(-12)^a$
80	$(1.49 \pm 0.02)(-12)^a$ $(1.36 \pm 0.03)(-12)^b$
75	$(1.51 \pm 0.05)(-12)^a$ $(1.46 \pm 0.02)(-12)^b$

Compositions by mole fraction:

^a $2.02 \times 10^{-5} \text{ CD}_3\text{H}$, $6.97 \times 10^{-5} ^{12}\text{C}^{16}\text{O}$, $4.92 \times 10^{-2} \text{ H}_2$, balance Ar. Pressure 90–380 Torr.

^b $5.96 \times 10^{-5} \text{ CD}_3\text{H}$, $6.02 \times 10^{-5} ^{12}\text{C}^{16}\text{O}$, $1.49 \times 10^{-1} \text{ H}_2$, balance Ar. Pressure 125 Torr.

Note: $(A \pm B)(-C) = (A \pm B) \times 10^{-C}$.

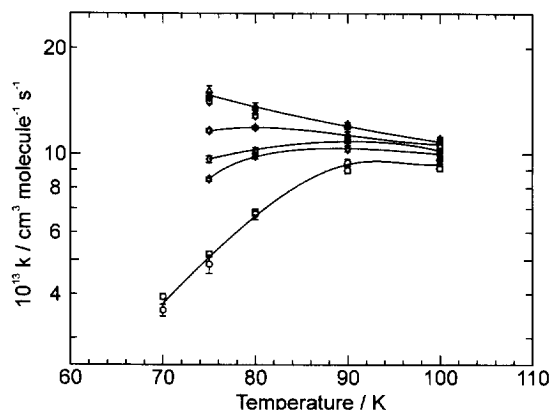


Fig. 2. The dependence of the rate constants for the vibrational deactivation of $^{12}\text{C}^{16}\text{O}(v=1)$ by CD_3H on the buffer gas composition: Ne/Ar buffer gas mixtures, —. Compositions (Ne:Ar ratio), with decreasing rate constants at 75 K, are 0:1, 1:4, and 1:1 (all 3 are top line), 4:1, 9:1, 20:1 and 1:0.

Table 5

The dependence of the rate constants for the vibrational deactivation of $^{12}\text{C}^{16}\text{O}(v=1)$ by CD_3H on the buffer gas: argon/neon buffer gas mixtures with 20 Torr of hydrogen

Composition	$k_{12\text{C}^{16}\text{O}-\text{CD}_3\text{H}} / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$			
/ Torr				
$p_{\text{Ne}} : p_{\text{Ar}}$	$T = 100$	$T = 90$	$T = 80$	$T = 75$
0 : 104	$(1.09 \pm 0.02)(-12)^{\text{a}}$	$(1.20 \pm 0.03)(-12)^{\text{a}}$	$(1.36 \pm 0.03)(-12)^{\text{a}}$	$(1.46 \pm 0.02)(-12)^{\text{a}}$
22 : 83	$(1.01 \pm 0.01)(-12)^{\text{b}}$	$(1.13 \pm 0.03)(-12)^{\text{b}}$	$(1.28 \pm 0.02)(-12)^{\text{b}}$	$(1.40 \pm 0.02)(-12)^{\text{b}}$
52 : 54	$(1.10 \pm 0.02)(-12)^{\text{c}}$	$(1.21 \pm 0.02)(-12)^{\text{c}}$	$(1.33 \pm 0.03)(-12)^{\text{c}}$	$(1.33 \pm 0.03)(-12)^{\text{c}}$
83 : 21	$(9.9 \pm 0.3)(-13)^{\text{d}}$	$(1.09 \pm 0.02)(-12)^{\text{d}}$	$(1.19 \pm 0.01)(-12)^{\text{d}}$	$(1.16 \pm 0.02)(-12)^{\text{d}}$
93 : 11	$(1.05 \pm 0.02)(-12)^{\text{e}}$	$(1.10 \pm 0.02)(-12)^{\text{e}}$	$(1.02 \pm 0.02)(-12)^{\text{e}}$	$(9.7 \pm 0.2)(-13)^{\text{e}}$
99 : 98	$(1.08 \pm 0.03)(-12)^{\text{f}}$	$(1.20 \pm 0.02)(-12)^{\text{f}}$	$(1.33 \pm 0.02)(-12)^{\text{f}}$	$(1.40 \pm 0.01)(-12)^{\text{f}}$
101 : 5	$(1.01 \pm 0.03)(-12)^{\text{g}}$	$(1.03 \pm 0.02)(-12)^{\text{g}}$	$(9.9 \pm 0.2)(-13)^{\text{g}}$	$(8.5 \pm 0.1)(-13)^{\text{g}}$
107 : 6	$(1.03 \pm 0.03)(-12)^{\text{h}}$	$(1.09 \pm 0.02)(-12)^{\text{h}}$	$(1.0 \pm 0.2)(-12)^{\text{h}}$	$(8.7 \pm 0.2)(-13)^{\text{h}}$
105 : 0	$(9.6 \pm 0.3)(-13)^{\text{i}}$	$(9.4 \pm 0.2)(-13)^{\text{i}}$	$(6.7 \pm 0.2)(-13)^{\text{i}}$	$(4.9 \pm 0.3)(-13)^{\text{i}}$
108 : 0	$(9.1 \pm 0.2)(-13)^{\text{j}}$	$(9.0 \pm 0.2)(-13)^{\text{j}}$	$(6.8 \pm 0.1)(-13)^{\text{j}}$	$(5.2 \pm 0.1)(-13)^{\text{j}}$

Compositions by mole fraction:

^a $5.96 \times 10^{-5} \text{ CD}_3\text{H}$, $6.02 \times 10^{-5} ^{12}\text{C}^{16}\text{O}$, $1.49 \times 10^{-1} \text{ H}_2$, $8.39 \times 10^{-1} \text{ Ar}$.

^b $5.95 \times 10^{-5} \text{ CD}_3\text{H}$, $7.96 \times 10^{-5} ^{12}\text{C}^{16}\text{O}$, $1.48 \times 10^{-1} \text{ H}_2$, $6.64 \times 10^{-1} \text{ Ar}$, $1.74 \times 10^{-1} \text{ Ne}$.

^c $5.93 \times 10^{-5} \text{ CD}_3\text{H}$, $7.93 \times 10^{-5} ^{12}\text{C}^{16}\text{O}$, $1.48 \times 10^{-1} \text{ H}_2$, $4.12 \times 10^{-1} \text{ Ar}$, $4.27 \times 10^{-1} \text{ Ne}$.

^d $6.01 \times 10^{-5} \text{ CD}_3\text{H}$, $7.93 \times 10^{-5} ^{12}\text{C}^{16}\text{O}$, $1.50 \times 10^{-1} \text{ H}_2$, $1.67 \times 10^{-1} \text{ Ar}$, $6.69 \times 10^{-1} \text{ Ne}$.

^e $6.00 \times 10^{-5} \text{ CD}_3\text{H}$, $7.96 \times 10^{-5} ^{12}\text{C}^{16}\text{O}$, $1.49 \times 10^{-1} \text{ H}_2$, $8.86 \times 10^{-2} \text{ Ar}$, $7.49 \times 10^{-1} \text{ Ne}$.

^f $3.41 \times 10^{-5} \text{ CD}_3\text{H}$, $4.56 \times 10^{-5} ^{12}\text{C}^{16}\text{O}$, $8.48 \times 10^{-2} \text{ H}_2$, $4.53 \times 10^{-1} \text{ Ar}$, $4.55 \times 10^{-1} \text{ Ne}$.

^g $5.95 \times 10^{-5} \text{ CD}_3\text{H}$, $7.95 \times 10^{-5} ^{12}\text{C}^{16}\text{O}$, $1.47 \times 10^{-1} \text{ H}_2$, $4.24 \times 10^{-2} \text{ Ar}$, $7.96 \times 10^{-1} \text{ Ne}$.

^h $5.73 \times 10^{-5} \text{ CD}_3\text{H}$, $7.74 \times 10^{-5} ^{12}\text{C}^{16}\text{O}$, $1.41 \times 10^{-1} \text{ H}_2$, $4.17 \times 10^{-2} \text{ Ar}$, $8.04 \times 10^{-1} \text{ Ne}$.

ⁱ $5.91 \times 10^{-5} \text{ CD}_3\text{H}$, $6.03 \times 10^{-5} ^{12}\text{C}^{16}\text{O}$, $1.48 \times 10^{-1} \text{ H}_2$, $8.40 \times 10^{-1} \text{ Ne}$.

^j $5.81 \times 10^{-5} \text{ CD}_3\text{H}$, $7.56 \times 10^{-5} ^{12}\text{C}^{16}\text{O}$, $1.43 \times 10^{-1} \text{ H}_2$, $8.44 \times 10^{-1} \text{ Ne}$.

Total pressures: 124–133 Torr. Mixture ^g 218 Torr.

Note: $(A \pm B)(-C) = (A \pm B) \times 10^{-C}$.

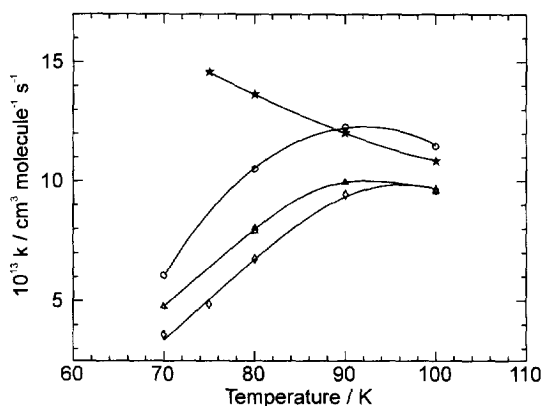


Fig. 3. A comparison of the rate constants measured in four buffer gases, all at a pressure of approximately 100 Torr. H₂ buffer gas: ○. He buffer gas with 20 Torr of hydrogen: △. Ne buffer gas with 20 Torr of hydrogen: ◇. Ar buffer gas with 20 Torr of hydrogen: ★.

rate constants measured in a mixture which contains 99 Torr of neon and 98 Torr of argon. If an argon atom is simply a spectator of the collisional process, then for a mixture with 99 Torr of neon, the rate constants should fall dramatically with decrease in temperature below 85 K. However, they do not: they rise in good agreement with the rate constants measured for the (VV) transfer in pure argon.

5. Discussion

The downturns in rate constants are increasingly steep for the system buffered in H₂, He and Ne respectively at the same pressure and a comparison of the rate constants measured in all four buffer gases at a pressure of approximately 100 Torr is shown in Fig. 3. At temperatures above 100 K the nature of the buffer gas has been shown to have no influence on the rate constants for the near-resonant (VV) energy transfer [1].

If the mechanism postulated for the downturn in rate constants is correct, the downturn should be steeper for larger mass third bodies since these are more effective in removing angular momentum from the orbiting collision and hence in stabilising the collision complex. Cross-sections have been measured for the rotational relaxation of CH₄ by He, Ne and Ar by Nesbitt and coworkers and an increase in

relaxation cross-section with increase in mass of the collision partner was observed [18]. This trend is exhibited for the H₂, He and Ne buffers investigated here.

A pressure dependence is observed for the helium buffer gas with the increased collision frequency at higher pressures increasing the likelihood of stabilisation of the collision complex. At the lowest buffer gas pressure of 100 Torr at 85 K using the hard sphere collision diameters given in Ref. [2], the collision frequency is about 7×10^9 collisions/sec. If third body collisions are to occur, the orbiting collision must survive for approximately 1×10^{-10} s. From an elementary calculation using the hard sphere diameters of CO and CH₄ [2] and the reduced mass of the collision pair, the rotational period has been estimated as approximately 1×10^{-10} s for one complete orbit. Thus, the duration of the orbiting collision is of the correct order of magnitude for a third body collision to occur during its lifetime. No pressure dependence is observed in the rate constants measured in the neon buffer gas. It appears that the rate of stabilisation of the collision complex is sufficiently fast at a neon pressure of 100 Torr that a further increase in the collision frequency with neon atoms does not have any additional effect.

The role of third body collisions investigated in this work is reminiscent of that played by the solvent in energy transfer processes in cryogenic liquids. For near-resonant (VV) transfer between solute molecules, the solvent affects the rate constants if the time for energy transfer is comparable with the solvent-solute collision rate which is much larger in the liquid than in the gas phase [19].

The Lennard-Jones well depth for the CO-Ar dimer is 110 K while that for CO-Ne is 59 K, that for CO-H₂ is 64 K, and that for CO-He is 30 K [2]. The well depths for the CO-Ar and CD₃H-Ar dimers are considerably deeper than those for the other three buffer gases considered. At temperatures below 85 K, a significant proportion of CO will exist as CO-Ar dimers and CD₃H as CD₃H-Ar dimers. Consideration of the van der Waals radii of the monomers and the dimers suggests that the latter will have collisional cross-sections of approximately double those of the former [2]. This could explain the enhancement of the rate constants for the near-resonant (VV) transfer when buffered in argon, and the

reduction in the corresponding rate constants when buffered with lighter mass gases with shallower well depths.

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