

## DIFFUSION OF VIBRATIONALLY EXCITED MOLECULES

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A treatment is presented for the effect of intermolecular vibrational energy transfer on the diffusion coefficient of vibrationally excited molecules. An analytic treatment based on random walk statistics and a Monte Carlo type calculation have been performed. Both methods yield very similar results which correlate well with existing experimental studies. A hard sphere collision model is treated extensively with comparisons made to other intermolecular potentials. The results support the involvement of long range energy transfer in  $V \rightarrow V$  interactions. The effect of temperature on the diffusion coefficient of vibrationally excited molecules is calculated, with applications to the  $\text{CO}_2^* - \text{CO}_2$  system.

### 1. Introduction

The diffusion coefficient for vibrationally excited molecules diffusing through ground state molecules is readily obtainable from studies of vibrational deactivation of laser excited molecules [1-3]. The first system for which this type of diffusion coefficient was obtained was the  $\text{CO}_2^* - \text{CO}_2$  system [1]. The excited state diffusion coefficient measured in this way was observed to be smaller than the self-diffusion coefficient for molecules in the vibrational ground state. This behavior was confirmed in later studies and was also observed for the  $\text{N}_2\text{O}^* - \text{N}_2\text{O}$  system [2,4]. The decrease in diffusion coefficient was suggested to be caused by exchange of excitation in collisions or near collisions. The theory of near resonant long range energy transfer predicts that the probability for such events should be high [5]. The role of near resonant energy transfer has been confirmed indirectly by recent temperature dependent studies of diffusion in  $\text{CO}_2$  and  $\text{N}_2\text{O}$  [4]. The difference between the viscosity determined diffusion coefficient and the diffusion coefficient deduced from relaxation measurements decreases as a function of increasing temperature. This

would be expected if the difference resulted from near resonant long-range energy transfer processes since the probability of such processes is inversely proportional to temperature [6]. A similar type of process has been treated by Mason, Monchick, and Nyeland for the effect of exchange of rotational energy in polar gases on the observed thermal conductivity of these gases [7].

In this paper we demonstrate that the observed difference between the viscosity determined diffusion coefficient and the optically determined diffusion coefficient can be reproduced by a theoretical description involving classical dynamics and long range energy transfer. We have performed two types of calculations. First, an analytic expression was obtained which reproduces the observed difference between the classical diffusion coefficient and the excited state diffusion coefficient and reduces to the classical diffusion coefficient in the absence of energy transfer. Secondly, a Monte Carlo calculation was used as an independent check on the analytic solution and the diffusion coefficient calculated by this method also exhibits appropriate behavior with and without energy transfer.

### 2. Theory

A general approach to the problem should utilize a microscopic theory of transport properties of poly-

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atomic gases with internal degrees of freedom, or at least a semimicroscopic approach based on the Boltzmann equation. A Boltzmann equation treatment of an equivalent problem (the effect of rotational energy exchange on the observed thermal conductivity of polar gases) has been provided by Mason, Monchick, and Nyeland [7]. With the objective of presenting a simpler treatment and obtaining a simple explicit analytic result for the effect of vibrational energy transfer on the observed diffusion of vibrationally excited species, we adopt in this paper a highly simplified approach, which is, however, sufficient to account for the main experimental results obtained to date. The simplifying features are introduced by imposing the following two assumptions:

(1) The probability of energy transfer in a given collision depends only on the relative velocity and on the impact parameter of the collision.

(2) The interaction potential  $V(r)$  (for the elastic scattering process) between the two molecules is spherically symmetric and does not depend on the direction of approach.

In addition, the following calculation will be simplified by focusing on an excited molecule which moves with a thermal velocity and which suffers random collisions with similar unexcited molecules, taken to be at rest before the collision. In other words we describe an "average" excited molecule colliding with an "average" collision partner. It should be noted that considering only stationary colliding partners is not expected to be a very good approximation for the absolute diffusion coefficient. It tends to overestimate this coefficient by neglecting the fact that particles moving opposite to the motion of the "marked" particle are more effective in reducing the transport rate than those moving in the direction of motion of the "marked" particle. However, we are mainly interested in the ratio between diffusion coefficients (with and without energy transfer) and we expect the error to largely cancel for this ratio. Comparison with the Monte Carlo calculations described in the next section show this to be a reasonable procedure. In fact, even for the absolute value of the diffusion coefficient, the error involved in the Monte Carlo calculation in not giving the particles moving opposite to the marked particle extra weight over those moving in the same direction as the marked particle, was found to be within the statistical noise of our Monte Carlo computation ( $\pm 3\%$ ).

Finally we point out that at the pressure range considered in this work, only binary encounters are of importance and that vibrational-translational energy transfer as well as radiative relaxation processes are disregarded in this work.

Let  $q(b)$  be the probability for energy transfer in a collision with an impact parameter  $b$ .  $q(b)$  depends on temperature through its dependence on the average velocity. Let  $M$  be some radius such that  $q(b) = 0$  for  $b \geq M$ . Our assumption is that  $M$  is sufficiently small so that only binary collisions have significant probability. Focusing our attention on a given collision event between the excited particle X and a thermal particle A, which is characterized by an impact parameter  $b$ , the scattering angle (the angle between the relative velocities before and after the collision) is a function of  $b$ :  $\theta(b)$ . This angle is sufficient to characterize the outcome of the collisions since by our assumptions all directions in a plane perpendicular to the original velocity of X are equally probable. In terms of  $\theta(b)$ , the angles that the velocities  $v'_X$  and  $v'_A$  (after the collision) form with the initial velocity  $v_X$  are given by

$$\theta_X = \frac{1}{2}\theta(b), \quad \theta_A = \frac{1}{2}[\pi - \theta(b)], \quad (0 \leq \theta(b) \leq \pi). \quad (1)$$

Due to the possibility of energy transfer we can write the corresponding angle of the excited particle in the form

$$\theta_e(b) = \frac{1}{2}\theta(b), \quad \text{with probability } 1 - q(b), \\ = \frac{1}{2}[\pi - \theta(b)], \quad \text{with probability } q(b). \quad (2)$$

$\theta_e(b)$  is the angle between the directions of motion of the excited particle before and after the collision. The probability for having a particular impact parameter (in the range  $0 \dots M$ ) is given by

$$P(b) = 2b/M^2. \quad (3)$$

Hence the average scattering angle is given by

$$\langle \cos \theta_e \rangle = (2/M^2) \int_0^M db b \{ [1 - q(b)] \cos \frac{1}{2} \theta(b) \\ + q(b) \sin \frac{1}{2} \theta(b) \}.$$

This average angle is sufficient, within our model, to characterize the diffusion coefficient. The diffusion

coefficient is obtained in the form (see appendix A)

$$D = \frac{1}{3} \langle v \rangle \langle l \rangle (1 - \langle \cos \theta_e \rangle)^{-1} \\ = \langle v \rangle \langle l \rangle \left( 1 - (2/M^2) \int_0^M db b \{ [1 - q(b)] \right. \\ \left. \times \cos \frac{1}{2} \theta(b) + q(b) \sin \frac{1}{2} \theta(b) \} \right)^{-1}, \quad (5)$$

where  $\langle v \rangle$  and  $\langle l \rangle$  are the mean velocity and mean free path, respectively. The classical diffusion coefficient is obtained by putting  $q(b) = 0$  in this expression. The ratio of the observed ( $D_o$ ) to the classical ( $D_c$ ) diffusion coefficient is

$$D_o/D_c = \left( 1 - (2/M^2) \int_0^M db b \cos \frac{1}{2} \theta(b) \right) \\ \times \left( 1 - (2/M^2) \int_0^M db b \{ [1 - q(b)] \cos \frac{1}{2} \theta(b) \right. \\ \left. + q(b) \sin \frac{1}{2} \theta(b) \} \right)^{-1}, \quad (6)$$

which constitutes our final result. This result can be shown to be independent of the arbitrary upper limit  $M$ . To obtain this ratio we must know  $q(b)$  for the particular temperature considered and  $\theta(b)$  which is determined by the intermolecular potential  $V(r)$ .

Explicit results can now be calculated for a hard sphere model. Let

$$V(r) = \infty, \quad \text{for } r \leq R, \\ = 0, \quad \text{for } r > R, \quad (7)$$

and

$$q(b) = q, \quad \text{for } r \leq d, \\ = 0, \quad \text{for } r > d. \quad (q \leq 1) \quad (8)$$

Eq. (7) implies

$$\theta(b) = 2 \arccos (b/R), \quad b \leq R, \\ = 0, \quad b > R. \quad (9)$$

With these results we obtain from eq. (6)

$$\frac{D_o}{D_c} = \left\{ 1 + 3q \left[ \left( \frac{d}{R} \right)^2 - 1 \right] \right\}^{-1}, \quad d \geq R, \quad (10a)$$

$$= \left\{ 1 - \left( \frac{d}{R} \right)^3 - \left( 1 - \left( \frac{d}{R} \right)^2 \right)^{3/2} \right\}^{-1}, \quad d \leq R. \quad (10b)$$

The following comments are now in order:

(a) The results given in eqs. (6) and (10) provide the approximate ratio between a self-diffusion coefficient modified by energy transfer,  $D_o$ , and the classical self-diffusion coefficient, in the absence of energy transfer,  $D_c$ . The result in eq. (6) was obtained for a general case with spherically-symmetrical elastic interaction and energy transfer probability while eq. (10) describes the special case of a hard sphere model defined by eqs. (7), (8).

(b) In general  $D_o$  can be either larger or smaller than  $D_c$ , the particular case is determined by the details of the functions  $\theta(b)$  and  $q(b)$ . For the hard spheres model  $D_o = D_c$  for  $d = 0, R$  for any  $q$ , and of course for  $q = 0$ .  $D_c > D_o$  for  $d > R$  and  $D_o > D_c$  for  $0 < d < R$ . The ratio  $D_o/D_c$  has a maximum as a function of  $(d/R)$  which from eq. (10b) is obtained for  $d/R = \frac{1}{2}\sqrt{2}$ . It is interesting to note that the position of this maximum does not depend on  $q$ . This position is in excellent agreement with the results of the Monte Carlo calculations as displayed in fig. 1.

(c) It is easy to understand qualitatively the variation of the ratio  $D_o/D_c$  as a function of  $d/R$ . For  $d > R$  grazing collisions (with impact parameter  $b$  greater than  $R$ ) which in the classical case have no effect on the propagation of the marked particle now have a finite probability of effectively changing its direction of propagation through energy transfer to the collision partner. For  $d > R$ , almost head-on collisions, which in the classical case lead to a reversal in the motion of the marked par-

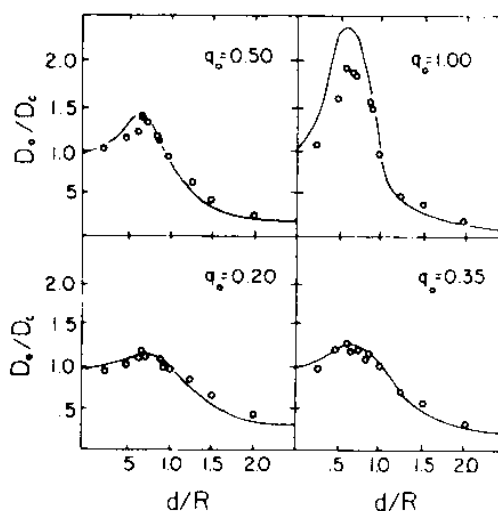


Fig. 1. Comparison of analytic expression eq. (10) to the Monte Carlo calculations as a function of  $d/R$  at various values of  $q$ . The same energy transfer potential and dynamics were used for both cases. Circles are the Monte Carlo calculation.

particle now have a finite probability of not perturbing the motion of the excited particle. The first case, in which excitation can be transferred without momentum transfer leads to a reduction in the observed diffusion coefficient while the second case in which excitation transfer must be accompanied with a substantial momentum transfer leads to an increase of the diffusion coefficient. Of course when  $d \rightarrow 0$ ,  $D_o \rightarrow D_c$  because the probability of energy transfer becomes negligible. Hence we should expect a maximum in  $D_o$  for  $0 < d < R$ .

(d) The ratio  $D_o/D_c$  is temperature dependent. Temperature comes in through the temperature dependence of the function  $q(b)$ . In the hard sphere model this can be expressed by taking either (or both)  $q$  or the transfer radius  $d$  as temperature dependent. Usually one assumes for this model a temperature dependence of  $q$  in the form  $q = q(T) = q_0/T$  where  $q_0$  is independent of  $T$ .

(e) Eqs. (6) and (10) were obtained by invoking some simplifying assumptions which were described above. The agreement between the result (10) and the Monte Carlo calculations which are not subjected to these approximations suggests that the general result can be used with a reasonable amount of confidence.

### 3. Monte Carlo calculation

A Monte Carlo approach was utilized to model the dynamics of molecular encounters. A vibrationally excited molecule X is chosen with velocity vector  $\mathbf{v}_X$  with arbitrary direction and a magnitude  $v_X$  characterized by the Boltzmann probability distribution

$$P(v_X) = 4\pi v_X^2 \left( \frac{m}{2\pi kT} \right)^{3/2} \exp\left( -\frac{mv_X^2}{2kT} \right), \quad v \geq 0. \quad (11)$$

The excited molecule encounters a collision partner at a distance  $l$  which is characterized by a Poisson distribution

$$P(l) = (1/\lambda) e^{-l/\lambda}, \quad (12)$$

where  $\lambda$  is the mean free path. The probability distribution for the impact parameter  $b$  is given by

$$P(b) = 2b/[\text{Max}(R, d)]^2, \quad 0 \leq b \leq \text{Max}(R, d) \quad (13)$$

where  $\text{Max}(R, d)$  is the larger of  $(R, d)$ . Finally, the velocity of the collision partner A is a random vector with a Boltzmann probability describing its magnitude and directional angles given by

$$P(\theta) = 1/\pi, \quad (14)$$

$$P(\varphi) = 1/2\pi. \quad (15)$$

A local orthogonal system is constructed with  $z_i$  (the  $z$  axis used in the calculation of the outcome of the  $i$ th collision) taken in the direction of  $\mathbf{u}$ , the relative velocity vector of the colliding pair. Let  $\mathbf{u}'_i$  be the relative velocity vector after the  $i$ th collision. Its magnitude is equal to that of  $\mathbf{u}$  and its direction in the local coordinate system defined here is given by  $\theta_i$  and  $\varphi_i$ .  $\theta_i$  is given by the equation

$$\theta_i = \begin{cases} 2 \arcsin(b_i/R), & \text{if } b_i \leq R, \\ 0, & \text{if } R < b_i \leq d, \end{cases} \quad (16)$$

for  $d > R$  with  $b_i$  distributed according to eq. (13) and  $\varphi_i$  distributed as in eq. (15). The second condition in eq. (16) corresponds to the possibility of energy transfer at distances larger than the hard sphere radius. The vector  $\mathbf{u}'$  found in this way should then be expressed in an external coordinate system by an appropriate rotation. Finally, the velocities after the collision are given by eqs. (17) and (18):

$$\mathbf{v}'_X = (\mathbf{v}_X + \mathbf{v}_A + \mathbf{u}')/2, \quad (17)$$

$$\mathbf{v}'_A = (\mathbf{v}_X + \mathbf{v}_A - \mathbf{u}')/2. \quad (18)$$

Encounters with an impact parameter less than or equal to the maximum diameter for energy transfers have a probability of  $q$  for energy transfer. The velocity of the excited molecule after the encounter is then taken as  $\mathbf{v}'_X$  with probability  $1 - q$  and  $\mathbf{v}'_A$  with probability  $q$ . If  $b > d$  then the velocity of the excited molecule is  $\mathbf{v}_X$  with probability 1.

### 4. The relative diffusion coefficient

The Monte Carlo routine was allowed to run for a time equal to approximately 60 collisions of a given initial molecule. The resulting square of the end to end distance was averaged over 500 such trajectories and the diffusion coefficient calculated from eq. (A.8). When there is no energy transfer or when  $d/r = 1$  or

result agrees with the classically determined self-diffusion coefficient within 9% [8].

With  $q = 0$ , we have observed the dependence of the diffusion coefficient  $D$  on the temperature  $T$ , pressure  $P$ , hard sphere radius  $R$ , and the mass  $m$ . We find that the dependences, within statistical error, are exactly what would be expected for a normal diffusion coefficient  $D \propto T^{3/2}, p^{-1}, R^{-2}$ , and  $m^{-1/2}$ . We see from the eq. (10) that the ratio of  $D_o/D_c$  depends only on  $q$  and the ratio ( $d/R$ ). This was checked with the Monte Carlo program and also found to be correct within statistical error. Thus we can express the variation in the ratio of  $D_o/D_c$  as a function of  $q$  and of the  $d/R$  ratio.

The dependence of  $D_o/D_c$  is illustrated in fig. 1 and 2. Plotted in fig. 1 is both the expression of eq. (10) and the Monte Carlo calculation for  $D_o/D_c$ .

## 5. Discussion

Expression (6) for the ratio  $D_o/D_c$  and our Monte Carlo calculations enable us to discuss the observed diffusion coefficient for an excited molecule for any given spherical model for the energy transfer probability.

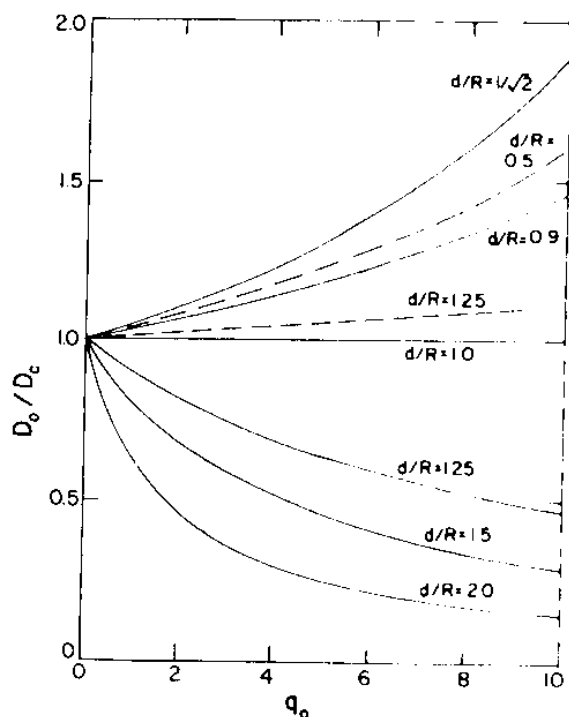


Fig. 2. Monte Carlo calculation of diffusion coefficient ratio as a function of  $q$  and  $d/R$ . Values of  $q > 0.5$  are shown for completeness.

A number of suggested models have been offered in the existing literature dealing with long range energy transfer [6,9,10]. However, due to a lack of detailed knowledge of  $q(b)$  as a function of  $b$ , there is little to suggest the most appropriate model.

$D_o/D_c$  has been calculated for three model energy transfer potentials in addition to the previously considered "hard sphere" energy transfer potential model. These energy transfer potentials are indicated in fig. 3. The given potential together with

$$\cos \frac{1}{2}\theta(b) = b/R \quad \text{and} \quad \sin \frac{1}{2}\theta(b) = \sqrt{1 - (b/R)^2}, \quad b \leq R, \quad (19a)$$

and

$$\cos \frac{1}{2}\theta(b) = 1 \quad \sin \frac{1}{2}\theta(b) = 0, \quad b > R, \quad (19b)$$

allow  $D_o/D_c$  to be calculated from expression (6).

$D_o/D_c$  for the potential used in fig. 3a is given by eq. (10). For the other energy transfer potentials, figs. 3b–3d, eq. (6) yields:

$$\text{fig. 3b} \quad D_o/D_c = \{1 + 3q - 3q(R)R^2/M^2\}^{-1},$$

$$\text{fig. 3c} \quad D_o/D_c = \{1 + \frac{1}{5} [17q(R) - 2q(0)] - 3q(R)R^2/M^2\}^{-1},$$

$$\text{fig. 3d} \quad D_o/D_c = \{1 + 3.24q(R) - 0.244q(0) - 3q(R)R^2/M^2\}^{-1}.$$

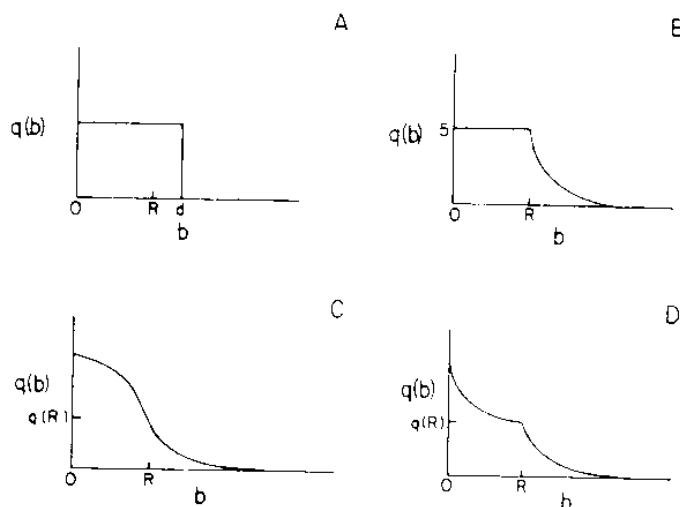
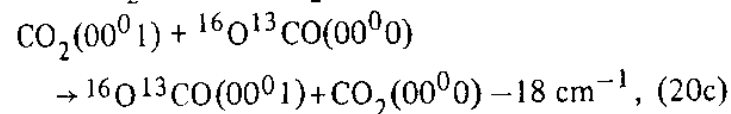
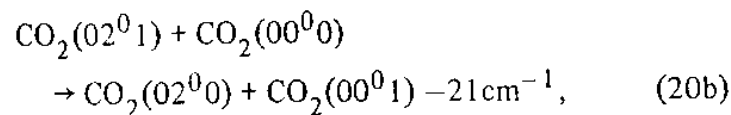
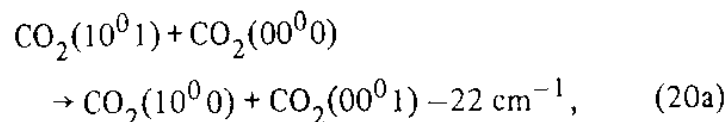


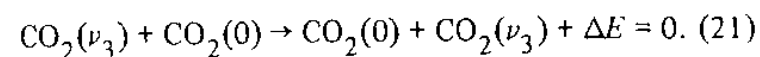
Fig. 3. Models for probabilities of energy transfer as a function of impact parameter.

In each of these cases  $M$  is included to allow for arbitrary termination of the potential at some distance greater than the hard sphere radius.

Each of the four potentials in fig. 3 produces values of  $D_o/D_c$  for  $\text{CO}_2$  close to the experimental value when reasonable values of  $\text{CO}_2$  energy transfer parameters,  $q(0)$  and  $q(R)$ , are used. In addition to the ratio  $D_o/D_c$  we can calculate a value for the energy transfer cross section due to long range energy transfer. (Ideally, this could then be used as an additional check on the chosen model.) Unfortunately, experimentally it is difficult to determine the cross section for an exactly resonant exchange of  $\nu_3$  quanta between  $\text{CO}_2$  molecules. However, slightly non-resonant processes involving exchange of  $\nu_3$  quanta have been measured. For each of the processes



a cross section of  $\sim 1/2$  gas kinetic has been experimentally determined [11,12] while the calculated cross sections are approximately gas kinetic [5]. It is apparent from these and a number of other measurements that theory consistently overestimates probabilities of energy transfer in resonant or near resonant encounters [12]. This has also been suggested in the development of the theory [5]. Using a development similar to Sharma's [6], we have calculated the cross section for the resonant process important in vibrational energy diffusion and obtain a cross section of  $55 \text{ \AA}^2$  for



However, due to the overestimates observed in previous work, this should be regarded as an upper limit and the cross section for resonant exchange of  $\nu_3$  quanta is probably much closer to the measured value of  $\sim 0.5$  gas kinetic observed for the similar almost resonant processes (20a-c). However, since (21) is exactly resonant, we will view  $\sigma = 0.5$  gas kinetic as a lower limit, yielding a range for the cross section between 0.5 and 1.1 gas kinetic for (21). While this provides some limit

on the range of reasonable energy transfer parameters, it does not provide sufficiently rigid restriction to allow a unique choice of parameters for a given energy transfer potential model. We also know that the limitation  $q(b) \leq 1/2$  for all  $b$  applies for a resonant process. For some  $b$ , where  $b < R$ , theory may formally yield  $q(b) > 0.5$  in which case it is assumed that  $q(b) = 0.5$ . One simplified model of the energy transfer potential is shown in fig. 3b. In this case  $q(b) = 0.5$  for all  $b \leq R$  and  $q = q(R)(R/b)^4$  for  $b > R$ . For this model we find that if we desire to match the experimental value of  $D_o/D_c = 0.83$  at 300 K [4] we must truncate the potential at  $b = 4.3 \text{ \AA}$ ,  $d/R = 1.075$ . Under these conditions,  $\sigma = 0.57$  gas kinetic. For potential 3c we must choose an additional parameter,  $q(R)$ . If we do not truncate the potential, and require  $q(0) = 0.5$  we find that  $q(R) = 0.1$  if  $D_o/D_c$  is equal to 0.83. This gives  $\sigma = 0.4$  somewhat smaller than desired with  $q(R)$  also somewhat smaller than would be expected from calculations. (Actually from our calculations we obtain  $q(R) = 0.4$  and  $q(0) = 0.5$ .) For model 3d we find that if we get  $q(0) = 0.5$  and require  $D_o/D_c = 0.83$  then  $q(R) = 0.1$ . In this case  $\sigma = 0.17$  gas kinetic, far smaller than expected. For potential 3a, the "hard sphere" model we have certainly oversimplified the situation in terms of energy transfer. In this case  $q$  must be some sort of average  $q$  and would not be expected to be 0.5 but must be  $0.5 > q$ . Thus we now have two parameters ( $q$  and  $d/R$ ) which we can vary to match the observed  $D_o/D_c$ . Of course we can ask what value do we get for the energy transfer cross section but even within reasonable ranges of  $\sigma$  we still have many choices of  $q$  and the  $d/R$  ratio. The temperature dependence of the  $d/R$  ratio can then be used as another parameter. Fig. 4 shows a plot of the experimental points as determined in ref. [4]. Drawn in is a line whose shape is given by the computation of  $D_o/D_c$  via eq. (10) with  $q = q_{300\text{K}}(300/T)$ . We find that the shape and the magnitude of  $D_o/D_c$  can be duplicated by a variety of  $d/R$  values and corresponding  $q$ 's. However, when we require an appropriate value of  $\sigma$ , we find that  $q = 0.45$ ,  $d/R = 1.07$  does give the reasonable value of  $\sigma = 0.51$  and has the necessary temperature dependence. It should be emphasized, however, that for every value of  $q \geq 0.43$  we can choose a  $d/R$  value which gives  $\sigma \geq 0.5$  and has the appropriate value of  $D_o/D_c$  vs  $T$  so that it will fall on the line drawn in fig. 4.

It is obvious from the foregoing discussion that a variety of energy transfer potential models give reasonable

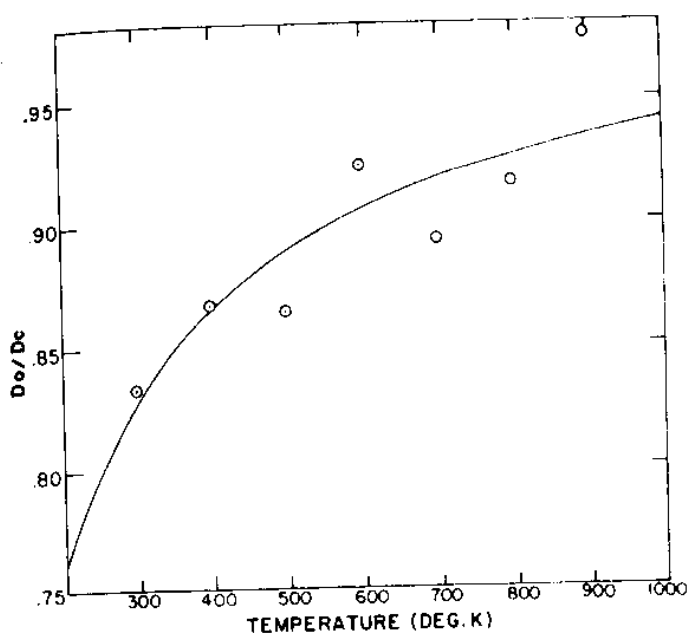


Fig. 4. Temperature dependence of the ratio of diffusion coefficients. Circles are experimental data of Doyennette et al. [4].

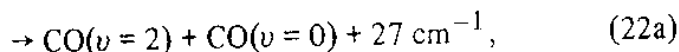
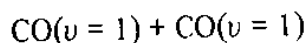
values of  $D_o/D_c$  and  $\sigma$ . However, it is certain that the actual  $q(b)$  is more complex than any model we have chosen. Unfortunately, our theoretical development does not appear sufficiently sensitive to the potential model to help us discriminate one model from the other. Partly this is true because total energy transfer cross sections are not accurately known for the desired resonant  $\text{CO}_2\text{--CO}_2$  process and additionally there is little detailed information as to the behavior of  $q(b)$  inside the hard sphere diameter. We have also assumed that the behavior of  $q(b)$  outside  $R$  is dictated by a dipole-dipole interaction. While this is likely the dominant interaction, it is also likely there are contributions, though small, from higher multipole moments.

Nevertheless, our model does duplicate the appropriate temperature dependence, and predicts quite reasonable values for  $D_o/D_c$  and  $\sigma$ .

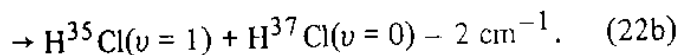
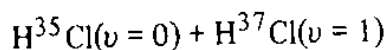
Useful tests for this model could be achieved by measuring the diffusion coefficient of a variety of different molecules. Information does exist on the diffusion coefficient of  $\text{N}_2\text{O}^*$  in  $\text{N}_2\text{O}$  [4]. However, the potential for this system is most likely similar to the  $\text{CO}_2^*\text{--CO}_2$  system. In addition the temperature dependent data has significant scatter. Thus this system does not afford a good opportunity for additional critical tests of our model. However, other systems may. We can say, in general, that systems having weak multi-

polar interactions or that are dominated by higher multipoles will have a value of  $D_o/D_c$  near 1 as long as  $q(b)$  for  $b < R$  is roughly constant or slowly varying within  $R$ . If interactions are dominated by strong dipolar forces and/or  $q(b)$  increases as  $b$  approaches  $R$ , we will see a  $D_o/D_c < 1$ . If very weak multipole forces are involved and  $q(b)$  is strongly peaked around  $b = 0$  we would expect  $D_o/D_c > 1$ . At present, however, there is little reason to believe that  $q(b)$  is anything but a constant or slowly varying function inside  $R$ .

Diffusion coefficients of molecules other than  $\text{CO}_2$  have been measured. These include  $\text{N}_2\text{O}^*$ ,  $\text{HCl}^*$ , and  $\text{CO}^*$  [3,4,13]. In the  $\text{N}_2\text{O}$  case a decrease in diffusion coefficient for vibrationally excited molecules is also noted, while for  $\text{HCl}^*$  and  $\text{CO}^*$ , the diffusion coefficients are virtually the same as the viscosity determined diffusion coefficient. This is to be expected and is predicted by our model. Rates have been measured for the following CO and HCl V-V processes.



and



For these almost resonant processes, 75 and 10 collisions are required, respectively [14,15]. This would lead to  $q(b)$ 's reduced by approximately these factors and correspondingly a  $D_o/D_c \rightarrow 1$ . For example, let us consider the "hard sphere" model for HCl. Assuming the potential has the same range as the  $\text{CO}_2$  potential, we find that for  $d/R = 1.07$  and  $\sigma = 0.1$ ,  $q = 0.09$ . For these parameters  $D_o/D_c = 0.96$ , which falls within experimental error of 1.

A previous attempt has been made to deduce diffusion coefficients of vibrationally excited molecules from thermal conductivity measurements [16]. While both treatments conclude  $D_o/D_c$  for CO should be  $\approx 1$ , the two treatments reach different conclusions as to the  $D_o/D_c$  values for  $\text{O}_2$  and  $\text{N}_2$  as well as the temperature dependence of  $D_o/D_c$  for  $\text{CO}_2$ . Experiment seems to bear out our temperature dependence and it is difficult to see how  $D_o/D_c$  for  $\text{N}_2$  could be substantially smaller than  $D_o/D_c$  for  $\text{CO}_2$  when V  $\rightarrow$  V transfer in  $\text{N}_2$  appears to take on the order of 100 collisions [17].

## 6. Conclusions

The results of modeling the diffusion coefficient of vibrationally excited molecules are in excellent qualitative and reasonable quantitative agreement with existing experiment. The observed difference in the diffusion coefficient for excited vs non-excited gases has its origin in near resonant energy transfer processes. However, before more detailed quantitative agreement can be achieved more data on the diffusion of vibrationally excited molecules is necessary as is more detailed knowledge about the intermolecular potential and parameters relevant to long range energy transfer.

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## Appendix A

The procedure employed in calculating the diffusion coefficient from the known probabilities for single collision events is quite common in the literature on random walk problems [19]. We briefly outline this procedure here. The mean square end to end distance for an  $n$ -step walk is

$$\langle L^2 \rangle = \left\langle \left( \sum_j r_j \right)^2 \right\rangle = \sum_j \langle r_j^2 \rangle + \sum_{j \neq j'} \langle r_j \cdot r_{j'} \rangle, \quad (\text{A.1})$$

where  $r_j$  is a vector describing the length and direction of the  $j$ th step. Because of the symmetry of the walk for large  $n$ , we can rewrite eq. (A.1) in the form

$$\langle L^2 \rangle = n \langle l^2 \rangle + 2n \sum_{j=1}^{\infty} \langle r_0 \cdot r_j \rangle, \quad n \rightarrow \infty. \quad (\text{A.2})$$

$l$  is a step length which is characterized by a Poisson distribution

$$P(l) = \langle l \rangle^{-1} \exp(-l/\langle l \rangle), \quad l = 0 \dots \infty, \quad (\text{A.3})$$

Therefore  $\langle l^2 \rangle = 2\langle l \rangle^2$  and

$$\langle L^2 \rangle = 2n \langle l \rangle^2 \left( 1 + (1/\langle l \rangle^2) \sum_{j=1}^{\infty} \langle r_j \cdot r_0 \rangle \right). \quad (\text{A.4})$$

For our problem, we assume that two consecutive steps are uncorrelated in their magnitude and direction, and where all directions of the azimuthal angle are equally probable it can be shown that [19]

$$(1/\langle l \rangle^2) \langle r_j \cdot r_0 \rangle = \langle \cos \theta \rangle^j \quad (\text{A.5})$$

and therefore

$$\langle L \rangle = 2n \langle l \rangle^2 (1 - \langle \cos \theta \rangle)^{-1}. \quad (\text{A.6})$$

If  $\langle v \rangle$  is the (thermal) velocity of the particle then

$$n \langle l \rangle = t \langle v \rangle, \quad (\text{A.7})$$

where  $t$  is the time for the  $n$ -step walk.

Finally, putting [20]

$$D = \langle L^2 \rangle / 6t \quad (\text{A.8})$$

we get eq. (5).

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