DIFFUSION OF OPTICALLY PUMPED MOLECULES AS A TOOL FOR PROBING THE INTERACTION OF EXCITED SPECIES

J. SIMONS

Chemistry Department, University of Utah, Salt Lake City, Utah 84112, USA

Received 28 March 1972

We have developed a theory to describe the diffusion of molecules whose internal-state populations are being perturbed by the application of intense pumping radiation. We show how to extract ground- and excited-state diffusion coefficients from experimental measurements carried out at several pumping intensities. Order-of-magnitude estimates of excited-state diffusion coefficients are presented, and the relation to the potential energy of interaction of excited species is discussed briefly.

1. Introduction

Transport property measurements have been used extensively to gain information about intermolecular forces [1]. Theoretical expressions containing the unknown intermolecular potential V are fitted to experimentally measured transport coefficients to evaluate parameters (e.g., ϵ and σ for a Lennard-Jones [1, p. 22] 6–12 potential) appearing in V.

In experiments which are carried out near or below room temperature, the population of excited electronic and vibrational levels is usually very low. Therefore, the measured transport properties are dominated by contributions involving the interaction of ground-state molecules. It is unlikely that much information about potential energy surfaces for excited-state species can be obtained from low temperature thermal experiments. However, if a specific excited electronic or vibrational level of the molecule were populated by, for example, optical pumping methods, then the transport properties would be influenced by both the ground- and excited-state potential energy surfaces[†].

In this paper, we treat the diffusion of molecules in which a specific electronic or vibrational state is being optically pumped[††]. The pumped molecules are allowed to diffuse down a tube containing a chemically inert buffer gas which does not interact with the pumping radiation. By assuming that the internal-state relaxation time is extremely small compared to the time scale of the diffusion experiment, we obtain compact expressions for the concentrations of excited- and ground-state species as functions of time. These expressions contain an *effective* diffusion coefficient which depends on the radiation density of the pumping field and the diffusion coefficients of the ground- and excited-states. The extraction of these latter diffusion coefficients from experimental data is discussed, and some order-of-magnitude estimates of the effects which are of interest here are presented.

2. Motivation

Let us consider the gas-phase diffusion (in the absence of pumping) of molecules of type A through non-reactive buffer molecules of type B. A sketch of one possible experimental arrangement is shown in fig. 1.

[†] For simplicity, we will treat only the lowest excited state. The extension to situations in which other states lie between the ground- and pumped states is reserved for a future publication.

[††] Not all molecules will permit the population of excited states by optical pumping. That is, frequently the excited-state lifetime is so short that currently-accessible pumping intensities are insufficient. Also, for some molecules, the non-radiative lifetime is sufficiently short to make significant the degradation of excitation energy into heat. We will neglect this complication here.

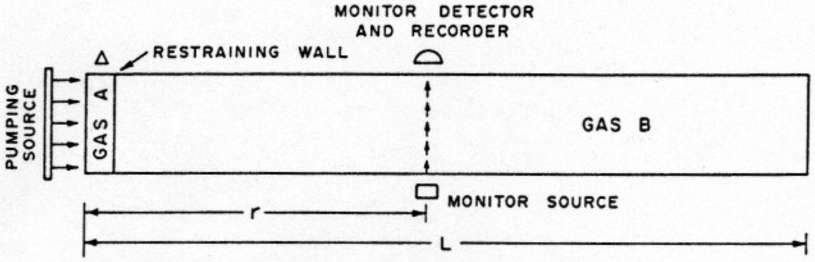

Fig. 1. Schematic of experimental setup for pumped diffusion measurements.

Initially, gas A is constrained to lie in a small segment $0 \leqslant X \leqslant \Delta$ of the diffusion tube, while gas B occupies the remainder of the tube. At $t = 0$ the restraining wall is removed and the concentration of species A is monitored[†] as a function of time, at a distance r (chosen for experimental convenience) from the origin. By using a tube whose length L is of the order of three to four times as long as the monitoring distance r, one can eliminate the problem of reflection at the boundary[††] $X = L$. Under these conditions, the monitored concentration of species A will vary in time as[≠]

$$C_A(r,t) = \tfrac{1}{2} C_A^0 \left\{ \operatorname{erf}\left[\frac{\Delta - r}{2(D_A t)^{1/2}}\right] + \operatorname{erf}\left[\frac{\Delta + r}{2(D_A t)^{1/2}}\right] \right\}, \qquad (1)$$

where C_A^0 is the initial concentration of A in the region $0 \leqslant X \leqslant \Delta$, and D_A is the diffusion coefficient of species A. The error function is defined by

$$\operatorname{erf}[z] = 2\pi^{-1/2} \int_0^z \exp(-y^2)\mathrm{d}y. \qquad (2)$$

For times satisfying

$$L^2/4D_A > t > r\Delta/2D_A \qquad (3)$$

and distances $r \gg \Delta$, the solution given in eq. (1) reduces to

$$C_A(r,t) = C_A^0 \Delta (\pi D_A t)^{-1/2} \exp(-r^2/4D_A t). \qquad (4)$$

Thus, by plotting the logarithm of $C_A t^{1/2}$ (monitored at point r) versus t^{-1}, one can determine the diffusion coefficient D_A. Of course, D_A is a function of the temperature of the two gases T and the pressure p (taken to be uniform throughout the tube):

$$D_A = 2.6280 \times 10^{-3} \, [T^3 (M_A + M_B)/2M_A M_B]^{1/2}, \times [p\sigma_{AB}^2 \Omega_{AB}^{(1,1)^*}(T_{AB}^*)]^{-1} \, \mathrm{cm}^2 \mathrm{sec}^{-1}, \qquad (5)$$

where the notation is described on page 539 of ref. [1]. The effects of the forces between pairs[‡] of A and B molecules are contained in σ_{AB} and the collision integral $\Omega_{AB}^{(1,1)^*}(T_{AB}^*)$, and it is through these quantities that experimentally determined diffusion coefficients are correlated with parameterized intermolecular potentials.

In the event that molecules of type A possess internal degrees of freedom, e.g., vibrational or electronic levels[‡‡], it is natural to inquire as to the physical meaning of a diffusion coefficient measured by the above method. Each internal state of molecule A should interact differently[≠≠] with molecules of type B, thereby giving rise to different diffusion coefficients for the various internal levels. An important question is: how is the experimentally measured diffusion coefficient related to the individual diffusion coefficients of the internal states? Intuitively, one expects that the

---

[†] We have in mind spectroscopic monitoring methods.

[††] Typical values which are experimentally reasonable are $r \approx 10$ cm, $L \approx 50$ cm, $\Delta \approx 0.5$ cm, diffusion coefficient ≈ 0.1 to 1 cm^{2}sec^{-1} for pressures of ≈ 0.1 to 1 atm.

[≠] A useful reference for the mathematics of diffusion is ref. [2].

[‡] The energy of interaction is assumed to be pairwise additive.

[‡‡] We will be concerned with electronic and vibrational levels here because it is in these cases that the room-temperature population of excited states is very low.

[≠≠] By excited-state potential surface we mean the potential energy of interaction of an excited molecule of type A with a ground state molecule of type B.

measured D_A will be essentially equal to the diffusion coefficient of the lowest internal state, if the higher states are negligibly populated[†] at the temperature of the experiment.

In this paper we consider the diffusion of molecules whose internal-state population is being perturbed by means of externally applied electromagnetic radiation of high intensity. We show how one can gain information about the interaction of excited species by measuring effective diffusion coefficients in an experiment in which an excited electronic or vibrational level is being pumped.

3. Pumped diffusion

We consider a diffusion experiment in which pumping radiation is applied to the complete diffusion tube (see fig. 1) both prior to and after the removal of the restraining wall at t=0. Experimentally, it is probably most reasonable to pass a beam of intense radiation down the axis of the diffusion tube. Of course, one must be careful to place the entire cross-sectional area of the tube in the beam so that diffusion into and out of the radiation field need not be considered. One should also check the attenuation of the beam to see whether absorption corrections need to be applied. In this paper we assume that attenuation is negligible and that the beam covers the total cross section of the tube.

Let us denote the local concentration of molecules of type A in the ground and pumped states by $n_1(r,t)$ and $n_2(r,t)$, respectively. The phenomenological equations governing these populations are taken to be

$$\mathrm{d}n_1(r,t)/\mathrm{d}t - D_1\nabla^2 n_1(r,t) = -Un_1 + Wn_2 \tag{6}$$

and

$$\mathrm{d}n_2(r,t)/\mathrm{d}t - D_2\nabla^2 n_2(r,t) = -Wn_2 + Un_1, \tag{7}$$

where D_1 and D_2 are the diffusion coefficients of the ground and excited states respectively[††]. The transition rate constants W and U are given in terms of the Einstein transition probabilities [3][‡] A and B, the radiation density $\rho(\epsilon)$ at the resonance energy $\epsilon = E_2 - E_1$, and the radiationless excitation (k_+) and de-excitation (k_-) rate constants[‡‡]:

$$U = k_+ + B\rho(\epsilon), \tag{8}$$

$$W = k_- + B\rho(\epsilon) + A. \tag{9}$$

Before t=0, the concentrations n_1 and n_2 are spatially uniform within $0 \leqslant r \leqslant \Delta$ and are equal to the steady-state values:

$$n_1^0 = N(k_- + A + B\rho)(2B\rho + A + k_- + k_+)^{-1}, \tag{10}$$

$$n_2^0 = N(k_+ + B\rho)(2B\rho + A + k_- + k_+)^{-1}, \tag{11}$$

where N is the total *initial* concentration[≠] of species A in $0 \leqslant r \leqslant \Delta$. Use of the equilibrium ratio n_2^e/n_1^e which attains in the absence of radiation[≠≠] ($\beta \equiv 1/kT$):

$$n_2^e/n_1^e = \exp(-\beta\epsilon) = k_+/(k_- + A), \tag{12}$$

allows eqs. (10) and (11) to be rewritten as follows:

$$n_1^0 = N[B\rho + k_+\exp(\beta\epsilon)]\,[2B\rho + k_+ + k_+\exp(\beta\epsilon)]^{-1} \tag{13}$$

$$n_2^0 = N(B\rho + k_+)[2B\rho + k_+ + k_+\exp(\beta\epsilon)]^{-1}. \tag{14}$$

To solve the pair of coupled diffusion equations [eqs. (6) and (7)], we Fourier transform the spatial dependence of $n_1(r,t)$ and $n_2(r,t)$, and we then use standard matrix techniques [5] to solve the resulting pair of first-order differential equations. By inverting the Fourier transforms of the solutions obtained in

---

[†] Which is the case for electronic or vibrational states of most molecules at room temperature.

[††] The boundary conditions are: $n_1(r,0) = n_1^0$ for $0 \leqslant r \leqslant \Delta$, $n_2(r,0) = n_2^0$ for $0 \leqslant r \leqslant \Delta$, $n_1(r,0) = n_2(r,0) = 0$ for $r > \Delta$. See eqs. (13) and (14) for definitions of n_1^0 and n_2^0.

[‡] For a straightforward discussion of kinetics of radiative processes, see ref. [4].

[‡‡] These phenomenological rate constants contain the effects of molecule–molecule and molecule–wall collisions as well as effects of internal non-radiative processes. The important assumption regarding k_+ and k_- is that they do not depend on the radiation density.

[≠] The total number of A molecules divided by the volume of the plug of length Δ.

[≠≠] It is assumed that ϵ has been measured.

this manner, one calculates the desired local concentrations as functions of time. Neglecting transient contributions[†] which decay to zero in a time of the order of $[2B\rho(\epsilon) + k_+ + k_+ \exp(\beta\epsilon)]^{-1}$ sec, the results are as follows:

$$n_1(r,t) = \frac{NW\Delta}{U+W}\left[1 - \frac{2Ud}{(U+W)^2}Q\right](\pi Dt)^{-1/2}\exp\left(-\frac{r^2}{4Dt}\right), \tag{15}$$

$$n_2(r,t) = \frac{NU\Delta}{U+W}\left[1 + \frac{2Wd}{(U+W)^2}Q\right](\pi Dt)^{-1/2}\exp\left(-\frac{r^2}{4Dt}\right), \tag{16}$$

with

$$d \equiv \tfrac{1}{2}(D_1 - D_2), \tag{17}$$

$$Q \equiv 3/2Dt - r^2/4D^2t^2, \tag{18}$$

and

$$D = \tfrac{1}{2}(D_1+D_2) - \tfrac{1}{2}(D_1-D_2)\frac{U-W}{U+W} = \frac{n_1^0}{N}D_1 + \frac{n_2^0}{N}D_2. \tag{19}$$

In eqs. (15) and (16), the terms involving Q can be shown to be insignificant for times greater than $[2B\rho(\epsilon) + k_+ + k_+ \exp(\epsilon\beta)]^{-1}$ sec, and so the above expressions simplify considerably to give:

$$n_1(r,t) = \frac{N\Delta W}{U+W}(\pi Dt)^{-1/2}\exp\left(-\frac{r^2}{4Dt}\right), \tag{20}$$

$$n_2(r,t) = \frac{N\Delta U}{U+W}(\pi Dt)^{-1/2}\exp\left(-\frac{r^2}{4Dt}\right). \tag{21}$$

Notice that the ground and excited states appear at the monitoring location *at the same rate* even though[††] $D_1 \neq D_2$, and that the *effective diffusion coefficient* D depends on the radiation density $\rho(\epsilon)$. Also, note that the ratio n_2/n_1 remains constant in space and time and is equal to the initial steady-state ratio n_2^0/n_1^0.

From eqs. (20) and (21) we see that by monitoring[‡] either the total concentration $n_1(r,t) + n_2(r,t)$ or one of the individual concentrations as a function of time, one can extract the effective diffusion coefficient D for any value of $\rho(\epsilon)$. For example, if the concentration of excited-state species is monitored spectroscopically (e.g., by looking at transitions from the pumped excited state to higher states), the effective diffusion coefficient can be obtained from the slope of a plot of $\ln[t^{1/2}\mathrm{OD}(r,t)]$ versus t^{-1}:

$$\text{slope} = -\frac{r^2}{4D} \text{ (see eq. (21)).} \tag{22}$$

$\mathrm{OD}(r,t)$ is the optical density ($\log I_0/I$) of the $2 \rightarrow$ higher state transition monitored at time t at a distance r from the tube origin.

Assuming that the effective diffusion coefficient has been obtained in the manner discussed above, let us now direct our attention toward the calculation of D_1 and D_2. From eqs. (8), (9), (12), and (19), we have

$$D(\rho) = \tfrac{1}{2}(D_1+D_2) + d\frac{k_+[1-\exp(-\beta\epsilon)]}{2B\rho\exp(-\beta\epsilon) + k_+[1+\exp(-\beta\epsilon)]}. \tag{23}$$

The effective diffusion coefficient in the absence of pumping radiation *can be measured* and is expressed[‡‡] as

$$D(0) = \tfrac{1}{2}(D_1+D_2) + d\left[\frac{1-\exp(-\beta\epsilon)}{1+\exp(-\beta\epsilon)}\right]. \tag{24}$$

Rearranging eqs. (23) and (24), one can derive the following important equation:

$$\left[\frac{1-\exp(-\beta\epsilon)}{1+\exp(-\beta\epsilon)}\right][D(0) - D(\rho)]^{-1} = d^{-1} + \frac{k_+}{2Bd}[1+\exp(\beta\epsilon)]\rho^{-1}. \tag{25}$$

A plot of the left side of eq. (25) versus the inverse of

[†] The validity of this step rests on the assumption that the time scale of internal-state transitions is much shorter than the time scale of the diffusion. Typically $[2B\rho + k_+ + k_+ \exp(\beta\epsilon)]^{-1} < 10^{-3}$ sec.

[††] Because the internal-state transition rate is so much faster than the diffusion rate, the initial steady-state populations n_1^0 and n_2^0 are maintained throughout the diffusion tube.

[‡] The monitoring technique will depend upon the properties of molecules A. One could monitor the absorption from the level pumped to a higher excited level. This can usually be done without appreciably altering the population of the pumped level.

[‡‡] If the pumped state is an excited electronic state, the factor $\exp(-\beta\epsilon)$ can probably be ignored.

the radiation density, yields the quantity d from the intercept[†]. Knowing both d and $D(0)$, eqs. (17) and (19) give D_1 and D_2 as

$$D_1 = D(0) + 2d[1 + \exp(-\beta\epsilon)]^{-1}\exp(-\beta\epsilon) \qquad (26)$$

and

$$D_2 = D(0) - 2d[1 + \exp(-\beta\epsilon)]^{-1}. \qquad (27)$$

With these equations, our task is now complete.

4. Summary and order-of-magnitude estimates

We have demonstrated how to obtain the effective diffusion coefficient by monitoring the appearance of either gound- or excited-state species. We have also shown how to calculate D_1 and D_2 from measurements of $D(\rho)$ at several different radiation densities. A knowledge of D_2 at various temperatures can then be used to evaluate parameters which appear in an intermolecular potential[††], by assuming a functional form for D_2 such as that given in eq. (5).

The usefulness of the experimental method described herein rests on the implicit assumption that the diffusion coefficient of the pumped state differs significantly from that of the ground state. Intuitively, one expects that the diffusion coefficient should depend on the "size" of the molecule; i.e., large molecules diffuse more slowly than small molecules. In table 1 we list the equilibrium internuclear separations of some ground- and excited-state diatomic molecules. From this table we see that differences in the "sizes" of ground and excited species of 10 to 20 percent are not uncommon.

To progress beyond simple intuition we have calculated approximate Lennard-Jones potential constants (σ) for the excited electronic states of some of the molecules listed in table 1. Scaling the ground-state potential constant σ by the ratio of sizes r_e^*/r_e (taken from table 1), we arrive at the results shown in table 2.

Table 1
Sizes (in Å) of ground- and excited-state molecules

Molecule	Ground and excited states	r_e[a)]	$r_e^{\text{excited}}/r_e^{\text{ground}}$
$Ba^{16}O$	$X^1\Sigma$ $A^1\Sigma$	1.940 2.134	1.10
$^9Be^{16}O$	$X^1\Sigma$ $A^1\Pi$	1.331 1.463	1.10
$^{35}Cl_2$	$X^1\Sigma_g^+$ $A^3\Pi_{0u}^+$	1.988 2.47	1.24
$^{12}C^{16}O$	$X^1\Sigma^+$ $A^1\Pi$	1.128 1.235	1.09
$^1H_2$	$X^1\Sigma_g^+$ $B^1\Sigma_u^+$	0.7416 1.293	1.74
$^{127}I_2$	$X^1\Sigma_g^+$ $B^3\Pi_{0u}$	2.666 3.016	1.13
$^{14}N_2$	$X^1\Sigma_g^+$ $a^1\Pi_g$	1.094 1.213	1.11

a) Ref. [6]. The excited-state "sizes" given here are probably underestimated with respect to the interaction of excited molecules. For further discussion, see ref. [7].

Table 2
Approximate potential constants (in Å) for excited states

Molecule	σ(ground state)[a)]	σ^*(excited state)[b)]
H_2	2.93	5.10
I_2	4.98	5.63
N_2	3.71	4.12
CO	3.76	4.10
Cl_2	4.40	5.46

a) Taken from pages 1110–1111 of ref. [1].
b) Calculated from $\sigma^* \approx \sigma(r_e^*/r_e)$.

These potential constants are appropriate for the description of the energy of interaction of two *identical* excited molecules. To predict the *mutual* diffusion coefficients, we must know the Lennard-Jones parameters ($\sigma_{12}^*, \epsilon_{12}^*$) for the interaction of an excited molecule of type 1 with a ground-state molecule of type 2. By rearranging the usual combining rules [1] $\sigma_{12} = \frac{1}{2}(\sigma_1+\sigma_2)$, $\sigma_{12}^* = \frac{1}{2}(\sigma_1^*+\sigma_2)$, we arrive at the expression which was used to calculate σ_{12}^*:

[†] The slope of such a plot might be used to study the nonradiative excitation rate constant k_+, in the event that the induced absorption probability B is known.

[††] The technique for extracting Lennard-Jones constants ϵ and σ from diffusion coefficient measurements is described on pages 580 and 562 of ref. [1].

Table 3
Approximate diffusion coefficients (in $cm^2 sec^{-1}$) for excited states at $T = 273.2°K$

Gas pair[a]	σ_{12}[b]	σ^*_{12}[c]	D_{12}	D^*_{12}[d]
H_2 in O_2	3.20	4.28	0.697	0.390
H_2 in CO	3.28	4.36	0.651	0.368
H_2 in CO_2	3.48	4.56	0.550	0.320
CO in O_2	3.51	3.68	0.185	0.168
N_2 in H_2	3.32	3.52	0.674	0.600
N_2 in O_2	3.56	3.76	0.181	0.162
N_2 in CO	3.64	3.84	0.192	0.172
N_2 in CO_2	3.84	4.04	0.144	0.130

[a] In each case the first molecule is the species being pumped.
[b] Taken from page 579 of ref. [1].
[c] Calculated from combining rule (e.g., page 567 of ref. [1]) $\sigma^*_{12} = \frac{1}{2}[2\sigma_{12} + \sigma^*_1 - \sigma_1]$.
[d] $D^*_{12} \approx D_{12}(\sigma_{12}/\sigma^*_{12})^2$. $P = 1$ atm.

$$\sigma^*_{12} = \tfrac{1}{2}(2\sigma_{12}+\sigma^*_1-\sigma_1). \tag{28}$$

To obtain the Lennard-Jones parameters σ^*_{12} shown in table 3, we have taken values of σ_{12} and σ_1 from ref. [1] and values of σ^*_1 from table 2, e.g., $\sigma^*_{H_2,O_2} = \frac{1}{2}[2(3.20) + 5.10 - 2.93] = 4.28$.

Finally, the excited-state diffusion coefficients D^*_{12} were calculated from [see eq. (5)] the equation $D^*_{12} \approx D_{12}(\sigma_{12}/\sigma^*_{12})^2$, which contains the assumption that the collision integrals $\Omega^{(1,1)}_{12}(T^*_{12})$ are approximately the same for ground- and excited-state molecules. This last assumption is of questionable validity, and future research efforts should be directed toward improving the equation used to predict D^*_{12}. In the absence of even approximate values for excited-state collision integrals, we can only hope that the values of D^*_{12} displayed in table 3 give some indication of the magnitude of the relative change $(D^*_{12}-D_{12})/D_{12}$ in the diffusion coefficient. Keeping the above limitations in mind, we see from table 3 that excited-state diffusion coefficients which differ from the ground-state coefficients by 10% are probably not uncommon†. Therefore, we conclude that there does exist the possibility of making practical use of the experimental technique discussed in this paper to probe the potential energy of interaction of electronically excited molecules. The case of vibrationally excited molecules is not as clear and is deserving of more study. Hopefully, the kind of experiment proposed here can be carried out in the near future, in this or another laboratory.

---

† A change of 10% means that the proposed measurements should be within the range of experimental accuracy. For excited vibrational levels, the magnitude of the change in diffusion coefficient is probably somewhat smaller than 10%.

References

[1] J.O. Hirschfelder, C.F. Curtiss and R.B. Bird, Molecular theory of gases and liquids (Wiley, New York, 1967).
[2] J. Crank, The mathematics of diffusion (Oxford Univ. Press, London, 1956).
[3] A. Einstein, Phys. Z. 18 (1917) 121.
[4] F. Pilar, Elementary quantum chemistry (McGraw-Hill, New York, 1968).
[5] F. Brauer and J.A. Nohel, Ordinary differential equations (Benjamin, New York, 1967) p. 276.
[6] G. Herzberg, Spectra of diatomic molecules (Van Nostrand, Princeton, 1950).
[7] J.O. Hirschfelder and M.A. Eliason, Ann. NY Acad. Sci. (1957) 451.