MEASUREMENT OF THE DIFFUSION COEFFICIENT OF ATOMIC CHLORINE IN MOLECULAR CHLORINE

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A scheme for measuring the diffusion coefficients of reactive atomic species through their radiative recombination reactions is proposed. The method was employed to measure the rate of diffusion of chlorine atoms in chlorine molecules and led to an observed value for the diffusion coefficient of 0.149 ± 0.025 $cm^2\ s^{-1}$ at 298 K and 1 atm.

1 Introduction

Diffusion coefficients and other transport properties of reactive atomic species are important in two respects:

(1) They are related to the intrinsic intermolecular potentials, and therefore, are valuable quantities in determining the interaction potentials between molecules or atoms [1].

(2) They are important data in macroscopic chemical kinetics, such as combustion and flames, and heterogeneous chemical reactions [2].

A number of techniques have been developed for measuring the diffusion coefficients of reactive atomic species In general, the atoms are generated either through microwave discharge or by laser photolysis The detection schemes range from classical methods, such as chemical reaction [3] and calorimetric [4] techniques, to instrumental methods, which include mass spectrometry [5], electron spin resonance spectrometry [6,7], resonance fluorimetry [8,9] and laser techniques [10,11].

Several authors [6,8] have employed the long-time solutions of the diffusion equation in analyzing experimental data and obtaining the diffusion coefficients. In this Letter, we report a method for measuring the diffusion coefficients of reactive atomic species through their radiative recombination reactions. The long-time behavior of the chemiluminescence intensity of the recombination reactions was solved It offers the advantage of being both straightforward in data acquisition and analysis and free from the limitation of temperature range imposed by most other detection techniques. Using the method, we measured the diffusion coefficient of chlorine atoms in chlorine molecules to be 0.149 ± 0.025 $cm^2\ s^{-1}$ at 298 K and 1 atm.

2. Theory

Consider the following generalized dissociation and radiative recombination reaction mechanism of homonuclear diatomic molecules [12–14].

$$X_2 \xrightarrow{\text{dissociation}} 2X(R, t), \tag{1}$$

$$X(R, t) \xrightarrow{D} X(R', t'), \tag{2}$$

$$X + X + M \xrightarrow{K_R} X_2^* + M, \tag{3}$$

$$X_2^* \xrightarrow{K_E} X_2 + h\nu, \tag{4}$$

$$X_2^* + M \xrightarrow{K_Q} X_2 + M. \tag{5}$$

Here, homonuclear diatomic molecules X_2 are dissociated into their atomic species X with a spatial and temporal distribution characterized by coordinates R and time t. The atoms X would diffuse through the medium with diffusion constant D and,

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meanwhile, with the help of a third body M, recombine with each other into their molecular electronic excited states X_2^*. The X_2^* would undergo photon emission or be quenched into a non-radiative state. Here, K_R, K_E, and K_Q represent the rate constants of recombination, photon emission, and third-body quenching processes respectively. In the present analysis, the contribution of the heterogeneous wall recombination reaction is neglected experimentally and theoretically.

For an instantaneous generation of a spatial distribution of X at $t = 0$, such as photodissociation by a short laser pulse, the temporal and spatial evolution of the X concentration is governed by the non-linear partial differential equation [2]

$$\partial n/\partial t = D\Delta n - K_R[M]n^2 , \quad (6)$$

where n is the concentration of X and Δ is the Laplacian operator. For a dissociation problem with cylindrical symmetry, where the spatial distribution is a function of radial coordinate r, the approximate solution is [2]

$$n(r, \theta, t) = N_0 \times \{1 + (K_R[M]N_0/8\pi D)\ln(1 + 4Dt/b^2)\}^{-1} \times [\pi(4Dt + b^2)]^{-1} \exp[-r^2/(4Dt + b^2)] . \quad (7)$$

Here b characterizes the spread of the initial distribution, θ is the polar angle of the cylindrical coordinates and N_0 is the concentration of X per unit length at $t = 0$. For an initial concentration distribution of

$$n(r, \theta, t = 0) = (N_0/\pi b^2)\exp(-r^2/b^2) , \quad (8)$$

eq. (7) becomes an exact solution

The local concentration of X_2^* follows a first-order time-dependent differential equation:

$$d[X_2^*](r, \theta, t)/dt = K_R[M][X]^2(r, \theta, t) - (K_E + K_Q[M])[X_2^*](r, \theta, t) , \quad (9)$$

where $[X_2^*](r, \theta, t)$ is the concentration of X_2^* at (r, θ, t), and $[X](r, \theta, t) = n(r, \theta, t)$. By solving eq. (9), the concentration of X_2^* per unit length at time t, $[X_2^*]_t$, is found to be

$$[X_2^*]_t = (K_R[M]N_0^2/2\pi)\exp[-(K_E + K_Q[M])t] \times \int_0^t \exp[(K_E + K_Q[M])t'] \{1 + (K_R[M]N_0/8\pi D) \times \ln(1 + 4Dt'/b^2)\}^{-2} [4Dt' + b^2]^{-1} dt' . \quad (10)$$

The observed chemiluminescence intensity of the above recombination reaction is then directly proportional to $[X_2^*]_t$.

Experimentally, one could measure [M], N_0 and b very accurately. However, the rate constant K_R, K_E and K_Q are known only for limited atomic species and third bodies [12–14]. In addition, eq. (10) is too complicated to be convenient for practical application. Nevertheless, knowing the range of the order of magnitudes of these rate constants, one could adjust [M] and N_0 experimentally, such that

$$(K_R[M]N_0/8\pi D)\ln(1 + 4Dt/b^2) \ll 1 .$$

We can obtain the following atom-diffusion-controlled solution for the recombination reaction in the long-time region

Let $y = t - t'$, $A = K_E + K_Q[M]$, $B = K_R[M]N_0^2/2\pi$, and $C = K_R[M]N_0$. Eq. (10) becomes

$$[X_2^*]_t \approx \frac{1}{4Dt + b^2}\frac{B}{A}(1 - e^{-At}) + \frac{4D}{(4Dt + b^2)^2}\frac{B}{A^2}[1 - e^{-At}(At + 1)] + \ldots . \quad (11)$$

In the case that the sum quenching and emission rate constants, $A = K_E + K_Q[M]$, is much greater than $4D/b^2$, one can obtain a good approximate solution in the long-time region:

$$[X_2^*]_t \simeq \frac{B}{A}\frac{1}{4Dt + b^2} . \quad (12)$$

The chemiluminescence decay behavior is then not correlated with the fluorescence lifetime and is directly proportional to $[X_2^*]_t$ of eq. (12). Moreover, eq. (12) indicates that under the conditions mentioned above, the long-time behavior of a radiative recombination reaction is completely controlled by the atomic diffusion process.

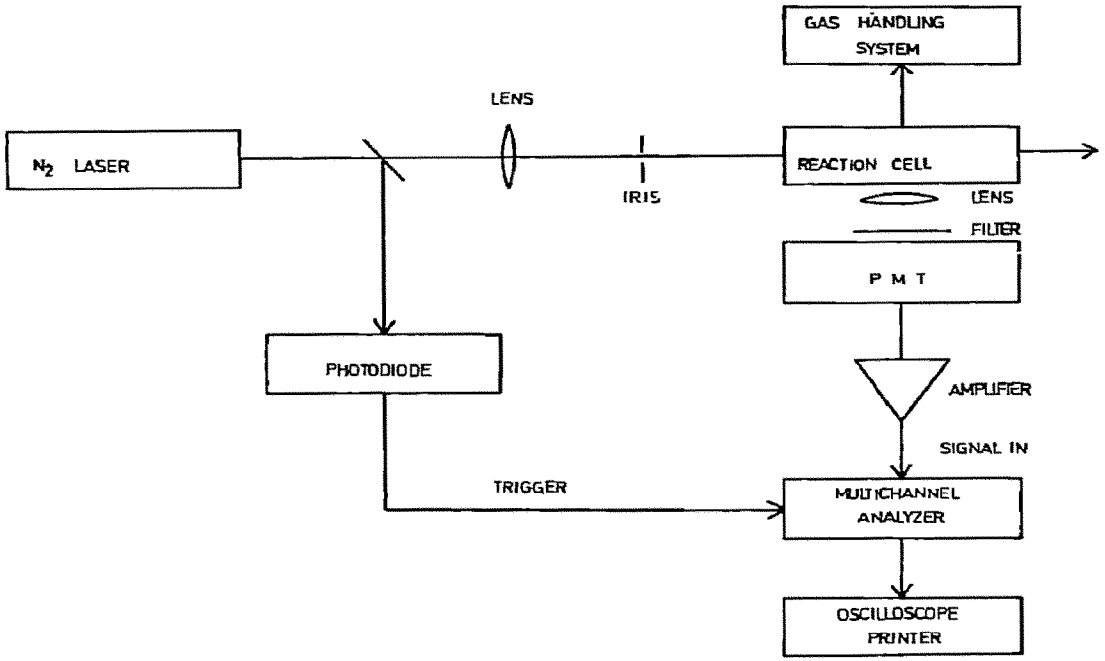

Fig. 1. Block diagram of the experimental arrangement of the chlorine atom recombination reaction. PMT represents photomultiplier tube.

3 Experimental

The experimental arrangement for chlorine atom recombination is in fig. 1. Chlorine atoms were generated through photodissociation of chlorine molecules by the 337 nm radiation of a home-made nitrogen laser (6 ns pulse width and 2 mJ pulse energy) The maximum intensity portion of the far field laser beam was focused (100 cm focal length lens) and spatially shaped with an iris. The usable laser energy was reduced to about 0.1 mJ per pulse. The cell was constructed from a 1 ℓ Pyrex flask fused with two glass side arms for laser passage. To reduce the scattering and reflection, two black graphitized Teflon light-buffers were inserted into the laser entrance port and one light trap was built in the exit port. Chlorine was introduced into the reaction cell through a vacuum system. The pressures were measured by a calibrated silicon oil manometer.

The chemiluminescence was collected through a side window by a lens and then filtered with a red long-pass filter. The photomultiplier signal (Hamamatsu type R446) was taken in the photon-counting mode and was, processed by a Nuclear Data 1100 multichannel analyzer with dwelling time of 100 μs. Signals from 500 to 1500 laser pulses were accumulated to enhance the signal-to-noise ratio.

4. Data analysis and results

The radiative recombination reaction of chlorine atoms in chlorine gas follows the generalized reaction mechanism outlined from eqs. (1)–(5) [12]. The K_R, K_Q and K_E values were measured or estimated to be of the order of 10^{15} cm^6 mol^{-2} s^{-1}, 10^{11} cm^3 mol^{-1} s^{-1}, and 10^4 s^{-1} respectively. Under the present experimental conditions $-N_0 \approx 10^{-10}$ mol cm^{-1}, $[Cl_2] \approx 10^{-6}$ mol cm^{-3} and $b = 0.29$ cm – one can numerically simulate the luminescence decay intensity by calculating the exact solution (10) and obtain the diffusion constant D Simultaneous calculation of eq. (12) showed that after 100 μs of the laser pulse, the approximate long-time solution generated essentially

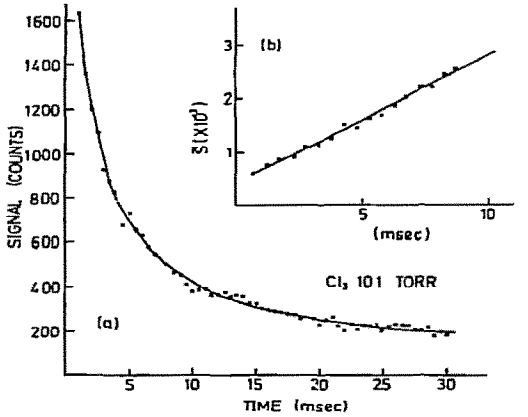

Fig. 2. Luminescence decay intensity of radiative recombination reaction of chlorine atoms in 10.1 Torr chlorine molecules. Each data point in (a) is the number of signal counts per 0.5 ms time channel averaged over a total of 920 laser firings The smooth line in (a) is the best non-linear fitting curve using eq. (13). The straight line in (b) is the best linear fit using eq. (14). See text for the parameter specification.

the same results as the exact solution This comparison justified the accuracy of the long-time approximate solution in analyzing the $Cl-Cl_2$ system.

As shown in fig. 2, each experimental point represents the photoelectron counts per 0.5 ms time interval. The photomultiplier signal $S(t)$ was fitted with either of the following two functional forms:

$$S(t) = C_1/(4Dt + b^2) + C_2 , \qquad (13)$$

$$\bar{S}(t) \equiv 1/[S(t) - C_2] = 4Dt/C_1 + b^2/C_1 , \qquad (14)$$

where C_1 represents the product of the instrumental factor, K_E and B/A of eq. (12) and C_2 is the photomultiplier background noise. For a given experimental b and C_2, the two fitting parameters, C_1 and D, were calculated by standard non-linear or linear least-squares routines.

In the present experiment, the b value was measured to be 0.29 ± 0.020 cm. The photomultiplier background noise taken after 450 ms of laser firing was measured to be 65 per 0.5 ms for fig. 2. From the non-linear least-squares fitting curve shown in fig. 2a, we obtained $D = 11.1$ cm^2 s^{-1} at a chlorine pressure of 10.1 Torr. The corresponding linear least-squares fitting curve shown in fig. 2b yields $D = 11.2$ cm^2 s^{-1}. Because of the inverse relation of eq. (14), the data points started to scatter considerably after the signal intensity decayed to about one fourth of its maximum value in fig. 2b. These scattering data points were neglected in the fitting procedure. A second measurement on a 15.1 Torr chlorine gas yields a corresponding diffusion constant of 7.60 cm^2 s^{-1}.

The projected average diffusion constant for chlorine atoms in chlorine molecules at 1 atm and 298 K is 0.149 ± 0.025 cm^2 s^{-1}. There are two major sources that contribute to the quoted error of the diffusion constant measurements. One is the accuracy of the measured b value. Its contribution to the error is estimated to be 0.020 cm^2 s^{-1}. The other source, which is responsible for an additional 0.005 cm^2 s^{-1} error, is the standard deviation of the least-squares curve fittings. If the chlorine pressure is too low, the luminescence detection system may fail to collect the same amount of the luminescent molecules as the atoms diffuse into a larger volume. In the present configuration and at a minimum of 10 Torr chlorine pressure, this source of error is negligible. Another possible complication comes from the initial high thermal energy of the chlorine atoms. Since local thermal relaxation takes place on a time scale of the mean collision time [15], which is of the order of 10 ns in the present experiment, this transient effect would cause an error much less than the quoted error of b.

5. Discussion

It is well known that atomic radiative recombination is not the only recombination pathway. For the chlorine case, the available evidence indicates that the non-radiative recombination makes up a substantial portion of the total recombination rate [12]. In this case, the modification one needs to carry out for the above calculation is substituting K_R with the overall recombination rate constant and normalizing K_E and K_Q by a proper weight. The rest of the theoretical analysis and the long-time decay behavior remain the same as the results obtained in section 2.

As shown by the halogen recombination experiments, there is the possibility that the quenching process,

$$X_2^* + X \rightarrow X_2 + X , \qquad (15)$$

and the three-body reaction,

$$X + M + M \rightleftharpoons XM + M , \quad (16)$$

are important. These processes would cause eqs (6) and (9) to be inadequate in describing halogen recombination reactions However, under present low atomic halogen concentration, which can be checked by varying the laser intensity, the contributions of these two processes are negligible.

During the photodissociation of chlorine molecules, one may generate a local temperature jump due to the initial high translational energy of chlorine atoms. By keeping the [M]/[X] ratio higher than 10^3, which can be achieved by controlling the laser power and/or M pressure, one can minimize the temperature jump to less than 4 K. Alternatively, one may just photodissociate molecules by a tunable laser with photon energy as close to the dissociation energy as possible.

The values of the diffusion coefficient for Cl—He and Cl—Ar systems have been reported to be 0.43 $\pm$ 0.01 $cm^2\ s^{-1}$ (1 atm, 300 K) and 0.26 $\pm$ 0.05 $cm^2\ s^{-1}$ (1 atm, 295 K) respectively in the literature [7,8]. Taking the collision diameters of He, Ar, and Cl_2 to be 2.58, 3.44, and 4.26 Å as obtained from ref. [1], and with the help of the Chapman—Enskog diffusion formula for a hard-sphere model, one can calculate the collision diameter of the chlorine atom in these three media, and obtain $\sigma_{Cl(He)} = 4.3$ Å, $\sigma_{Cl(Ar)} = 2.3$ Å and $\sigma_{Cl(Cl_2)} = 3.0$ Å. The diversity of the collision diameter of Cl in these three media indicates that the interaction between Cl and these three kinds of molecules cannot simply be described by normal van der Waals forces as exist between two simple nonpolar molecules For an open-shell atom like chlorine, this kind of irregularity is not unexpected. Temperature-dependent diffusion measurements or a crossed molecular beam experiments are needed to clarify these observations.

Further measurements of the diffusion constants of the chlorine atom in other inert molecules are under way and will be reported later.

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