Self-Diffusion in Gaseous Ammonia

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TABLE II. Data related to cross sections for molecular reorientation in some $D_{\infty h}$ molecules.

Molecule	σ_{eff} (Å^2)	σ_{kin} (Å^2)	$\sigma_{\text{kin}}/\sigma_{\text{eff}}$	V_Q (10^{16} ergs)	$\beta^2 \langle V_Q^2 \rangle^2 / \bar{v}^2$ (arbitrary units)
H_2	2.8	27	10	32.1	12.6
F_2	12	41	3.4	21.2	46.0
C_2H_2	64	53	0.8	129	42.1×10^3

In this Note, T_1 measurements are reported for the ^{19}F nuclei in the homonuclear diatomic gas F_2. Conventional magnetic resonance pulse techniques were employed as described in the earlier papers. The gas sample was obtained from Matheson of Canada, Ltd.; the stated minimum purity of the sample was 98.0%. Measurements were carried out at 222, 290, and 333°K. Experimental values of the second virial coefficients for F_2 [5] were used to convert the measured pressures to corresponding amagat densities. Each plot of T_1 vs ρ was linear to within experimental uncertainty over the range of densities studied (4-15 amagat). The experimental values of T_1/ρ and $(T_1/\rho)T^{3/2}$ are given in Table I. The essentially constant value of $(T_1/\rho)T^{3/2}$ indicates that the spin–rotation interaction dominates the relaxation process. The extremely short values of T_1 result from the large value of the spin–rotation constant for the F_2 molecule.

The kinetic theory of nuclear spin relaxation proposed by Gordon[6,7] yields the following expression for σ_{eff}, the cross section for the transfer of angular momentum during a collision:

$$\sigma_{\text{eff}} = \tfrac{2}{3}(C^2 I/\hbar^2 L)(\tfrac{1}{2}\pi\mu kT)^{1/2}(T_1/\rho),$$

where C is the spin–rotation constant, I the molecular moment of inertia, μ the reduced mass of a colliding pair of molecules, T the absolute temperature of the gas, and L the number of gas molecules per cubic centimeter at NTP. The experimental value for C is 157 kHz [8] and for I is 31.7×10^{-40} g·cm^2.[9] The deduced cross sections σ_{eff} are listed in Table I.

In Table II cross sections measured at 297°K for H_2,[10] F_2, and C_2H_2 [11] (all molecules of symmetry $D_{\infty h}$) are listed. We discuss this data in terms of the weak collision approximation. In this limit the cross sections are expected to be proportional to $\beta^2 \langle V_a^2 \rangle^2 / \bar{v}^2$, where $\beta \langle V_a^2 \rangle$ is the average anisotropic interaction energy and $\bar{v}$ the relative velocity of a colliding pair of molecules. The dominant contribution from the long-range part of the anisotropic potential comes from the quadrupole-quadrupole term V_Q in the multipole moment expansion in the interacting charge distributions[12]:

$$V_Q = 4\pi(14/5)^{1/2}(Q^2/R^5)$$
$$\times \sum_{\mu}(-)^\mu C(224, \mu-\mu 0) Y_{2\mu}(\Omega_1) Y_{2\mu}^*(\Omega_2),$$

where Q is the molecular quadrupole moment,[13] $C(224, \mu-\mu 0)$ is a Clebsch–Gordon coefficient, and

$Y_{2\mu}(\Omega)$ is a spherical harmonic. The V_Q and $\beta^2 \langle V_Q^2 \rangle^2 / \bar{v}^2$ values for $R = \sigma_0$, where σ_0 is the Lennard-Jones parameter, are given in Table II. Unfortunately there is no simple way to estimate the contribution to the cross sections of the short-range part of the anisotropic potential. The ratio $\sigma_{\text{kin}}/\sigma_{\text{eff}}$, where $\sigma_{\text{kin}} = \pi\sigma_0^2$ is the geometric cross section, provides a measure of the efficiency of collisions in causing the molecular rotational angular momentum to be randomized. Only for $\sigma_{\text{kin}}/\sigma_{\text{eff}} \gg 1$ is the weak-collision approximation strictly valid. From Table II we see that the approximation is a reasonable one for H_2 and F_2 but not for C_2H_2. A consideration of the tabulated values suggests that σ_{eff} increases in proportion to $\beta^2 \langle V_Q^2 \rangle^2 / \bar{v}^2$ so long as the weak-collision approximation is reasonable, and it increases much more slowly once the approximation becomes invalid. This behavior is as expected if the long-range forces play an important role in determining the cross section for molecular reorientation in these gases.

† Holder of a National Research Council of Canada Fellowship.
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Self-Diffusion in Gaseous Ammonia

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Although polar gases play an important role in modern technology relatively little study has been
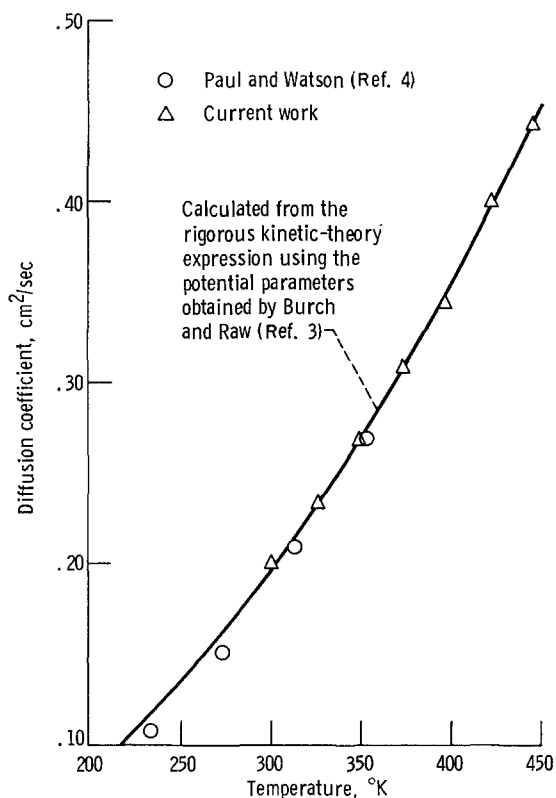
FIG. 1. Comparison of experimental self-diffusion coefficients for ammonia with theory and with literature values.

devoted to their transport properties, especially diffusion coefficients. Polar gases are generally difficult to work with and, in addition, the collision integrals necessary for theoretical calculation of these properties were not available until 1961.[1] Measurement of the self-diffusion coefficient (D_{11}) of a strongly polar gas over a range of temperatures should provide a test of the validity of simplifying assumptions[1] necessary for calculation of the collision integrals for strongly orientation-dependent potentials such as the Stockmayer potential. This note gives results of recent measurements of D_{11} for gaseous ammonia between 301.3 and 445.6°K.

Measurements were made in a stainless-steel Loschmidt-type cell with a shear interface quite similar to the one described by Strehlow.[2] The cell was mounted in a large oil bath maintained to within ±0.02°C. Temperatures were measured with a platinum resistance thermometer. The lower half-cell contained 10–15% $^{15}NH_3$ which served as a tracer. Following a diffusion run, the entire contents of each half-cell were removed by freezing with liquid nitrogen. Prior to mass spectrometric analysis each sample was completely decomposed over a heated ($\sim$1200°C) platinum filament. The ratio of $^{15}NH_3$ to $^{14}NH_3$ was then determined by scanning masses 28, 29, and 30. From these results the

mutual diffusion coefficient of $^{15}NH_3$ into $^{14}NH_3$ was calculated in the usual way[2] and an isotopic correction applied to give D_{11}.

The experimental results adjusted to 1 atm pressure are listed in Table I and shown graphically in Fig. 1. The value at each temperature is the average of at least three separate runs. Pressures varied between 408 and 729 torr. With the exception of the point at 397.3°K, the results are in excellent agreement with the theoretical curve calculated from rigorous kinetic theory using the Stockmayer potential parameters obtained by Burch and Raw from their recent viscosity data.[3] These theoretical results are also listed in column 3 of Table I. The only measurements of D_{11} for ammonia reported previously are those of Paul and Watson[4] using the two-bulb modification of the Loschmidt method. Their results are also shown on Fig. 1. Paul and Watson state that there is marked disagreement between observed and calculated values at low temperatures and explain this discrepancy in terms of dimerization. However, the current results show no tendency toward being low in the temperature range where the data overlap.

Table I also contains theoretical results obtained from rigorous kinetic theory using the Stockmayer potential parameters obtained by Monchick and Mason[1] from earlier viscosity data. With the exception of the results at 397.3 and 422.9°K, the experimental coefficients are seen to be equal to or to lie between the two theoretical values. The value at 397.3°K definitely appears inconsistent with both theory and the other experimental points. (The low results were probably caused by instability of the mass spectrometer during the analysis of these particular samples.)

The last column of Table I lists the results obtained from the viscosity data of Burch and Raw using the well-known relation: $\rho D_{11}/\eta = 6/5 \langle A_{11}^* \rangle$, where ρ is the

TABLE I. Comparison of experimental self-diffusion coefficients for ammonia with those calculated from viscosity data and from rigorous kinetic theory.[a]

Temperature, (°K)	D_{11} (Exptl)	D_{11} (Theoret)[b]	D_{11} (Theoret)[c]	D_{11} (Viscosity)[d]
301.3	0.200±0.001	0.200	0.198	0.195
326.4	0.233±0.002	0.235	0.233	0.230
348.7	0.268±0.001	0.269	0.266	0.264
373.8	0.308±0.003	0.309	0.305	0.305
397.3	0.343±0.002	0.350	0.345	0.346
422.9	0.399±0.003	0.397	0.391	0.393
445.6	0.441±0.001	0.441	0.434	0.438

[a] Units in square centimeters per second; pressure is 1 atm.
[b] Calculated using the Stockmayer potential parameters obtained by Burch and Raw: δ_{max}=0.68, ϵ/k=431°K, σ=2.99 Å.
[c] Calculated using the Stockmayer potential parameters obtained by Monchick and Mason: δ_{max}=0.70, ϵ/k=358°K, σ=3.15 Å.
[d] $\langle A_{11}^* \rangle$ values taken from Ref. 1 using the Stockmayer potential parameters given above in Footnote b.

density and η the viscosity. The quantity $\langle A_{11}{}^* \rangle$ is a ratio of collision integrals (essentially the ratio of the viscosity and diffusion cross sections) and is quite insensitive to temperature and the details of the intermolecular force law. Thus, the above equation yields D_{11} from experimental viscosity which is effectively independent of any molecular model. Diffusion coefficients calculated by this method are only slightly lower than the other values below 326.4°K, and are in excellent agreement above this temperature.

This research was undertaken to test the ability of current theory to predict the diffusion coefficient of polar gases. For the case of highly polar ammonia over the indicated temperature range, the above results demonstrate that the theory is indeed adequate.

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# Dual Photon Emission from the Chemiluminescent SO +O Reaction*

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The nitric oxide–oxygen atom reaction has been studied extensively over the last years[1] and clear evidence has been published that the light emission produced at low pressures is the result of a two-body collisional process.[2] Due to the complex nature of the reaction, however, there still is some dispute in the literature. The analogous mechanism for the reaction of SO and O to produce light emission is generally accepted.[3] In this paper evidence is presented that not one, but two photons are emitted in the SO+O reaction. Similar dual photon emission due to excited atoms is well known.[4]

The present results can be explained in terms of the following steps:

$$SO+O \rightarrow SO_2{}^* + h\nu_1, \qquad (1)$$

$$SO_2{}^* \rightarrow SO_2{}^{\ddagger} + h\nu_2. \qquad (2)$$
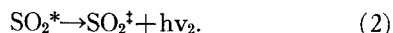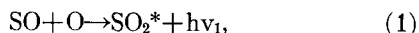
That is, a primary reaction involving the formation of SO_2 in an excited state with the loss of part of the energy of recombination due to photon emission followed by emission of the second photon from the excited state $(SO_2{}^*)$, to a lower level $(SO_2{}^{\ddagger})$ near the ground state.

The chemiluminescence was produced using either CS_2 or COS reacting with O atoms in a flow system at about 40 mtorr total pressure. Part of the flow was bypassed through a 4 mm i.d. Pyrex tube. A small section of this tube was between two 8575 RCA photomultipliers used as detectors. Each photon observed, produced a low amplitude fast pulse. The pulse output at the anode was amplified by a LeCroy 133 linear amplifier and directcoupled to a LeCroy 161 dual discriminator. The negative output pulses from the 161 discriminators were counted using Canberra 1492 scalers to obtain the single pulse rate from each photomultiplier. The positive outputs of the discriminators were coupled to a Canberra 840 coincidence analyzer where the output coincidence pulses were counted using a Canberra 871 scaler. Counting intervals were set via a Canberra 890 scaler/timer by the use of a gating pulse. The accidental coincidence rate using a light bulb was used to measure the resolving time of the coincidence circuit for various control settings. Most experiments were performed under conditions where approximately 10^6 counts/min were counted by each singles scaler. At this level an accidental coincidence rate of 833 counts/min, for example, corresponded to a resolving time of 25 nsec. With no light of any kind the random background pulses yielded a 5 counts/min coincidence.

The SO+O reaction produced dual photon emission observed as net coincidence counts above the accidental background rate. The ratio of this dual emission to background was found to decrease as resolving time increases. From this the average half-life time for the excited $SO_2{}^*$ species was determined to be $3(\pm 1) \times 10^{-8}$ sec.

The dual photon emission is estimated to be at least 10% of the total. A more precise determination is precluded at present by the limitations of geometry, spectral response, and counting efficiencies of the photomultipliers. This dual emission also is compatible with the absorption spectrum, the fluorescence[5] and the emission spectrum[6] of SO_2.

Using the present arrangement such dual emission could not be seen from NO+O reaction. The total energy of the two photons emitted from such a reaction cannot have an energy exceeding the exothermicity of the reaction, but may be somewhat less. The SO+O reaction is 5.6 eV exothermic[7] and if each photon would have the half, this would correspond to a wavelength of 4400 Å. If one photon is of higher energy, the second must be lower. In this study the 8575 RCA photomultiplier tubes used were sensitive from the uv region to about 6000 Å. Therefore many combinations of energy for the two quanta could be counted. However, the reaction of NO+O→NO$_2$ is 3.1 eV exothermic[8] and half would be 1.5_5 eV (~7900 Å) and could not be expected to be observed with these tubes. Indeed no coincidence effect above the accidental rate was found for the NO+O reaction, nor for the SO+O reaction if filters were used where the observed spectral region corresponded only to energies greater than 3.5 eV.