

The Role of the Rotational State in Intermolecular Interactions of H₂O with H₂ and CH₃Cl¹

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Rotational-state resolved measurements of H₂O-H₂ and H₂O-CH₃Cl intermolecular interactions were performed. Using light-induced drift as a tool, we measured changes in transport collision rate ν upon rovibrational (J, ν)-excitation of H₂O. We studied P- and R-branch excitation with J ranging from 0 through 9 for H₂O excited in the fundamental asymmetric stretch mode. Combination of P and R data yields the dependencies of ν upon rotational (J) and vibrational (ν) quantum numbers separately. For H₂O-CH₃Cl it is found that ν decreases by 25% as J increases from 0 to 9. For H₂O-H₂ the decrease is only 1.0%. These data seem to exemplify a fundamental aspect of dipole-dipole interaction: the familiar $1/r^3$ interaction term is highly J -dependent. This is attributed to the increasing averaging-out of the dipolar potential as the rotational quantum number increases.

KEY WORDS: Collision rate; dipole-dipole interaction; H₂O; light-induced drift; rotational state-dependent interaction.

1. INTRODUCTION

At the heart of the work that Ed Mason performed during his impressive scientific career was the connection between microscopic properties of molecules and the macroscopic behavior of a gas, i.e., between cross sections and transport properties. For ordinary transport properties—viscosity, diffusion, thermal conductivity—such cross sections are Boltzmann averages over the internal degrees of freedom. In recent years a transport effect has been explored in which cross sections for individual internal states are studied, *viz.*, light-induced drift (LID) [1, 2]. Indeed, it is precisely the internal-state dependence of the cross sections which is a

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prerequisite for the occurrence of LID. In this contribution, we present results on the rotational-state dependence of cross sections (more precisely transport collision rates) for systems which were extensively considered also by Mason and Monschick [3] some three decades ago, *viz.*, polar gas mixtures. It is shown that cross sections for a system like $\text{H}_2\text{O}-\text{CH}_3\text{Cl}$ decrease by more than 25% as the rotational quantum number increases from $J=0 \rightarrow 9$. This seems to reflect the increasing averaging-out of the familiar $1/r^3$ term in the dipole-dipole potential as the rotational period becomes shorter compared to the interaction time.

2. EXPERIMENTAL PROCEDURE

2.1. Principle of LID

The principle of LID is best explained by considering a low-pressure ($p \approx 100$ Pa) binary gas mixture contained in a closed tube. Let the mixture consist of light-absorbing molecules (a) and inert buffer molecules (b). Suppose that the gas is irradiated by narrow-band laser radiation tuned into a Doppler broadened absorption profile of the active species. Only those molecules will be excited whose velocity component along the \mathbf{k} vector of the laser field satisfies $v_k = v_L \equiv \Delta\omega/|\mathbf{k}|$, where $\Delta\omega$ is the laser frequency detuning from resonance. Hence, velocity selective excitation is achieved (see Fig. 1). If the collisional interaction of species a with respect to b is modified upon excitation, the gas will become kinetically anisotropic, and LID will occur. In a closed tube this produces a net concentration difference Δx_a over the tube. The magnitude of Δx_a is proportional to the relative change in collision rate $\Delta v/v$. Assuming infinite dilution of molecules a in b and assuming δ -peak excitation, we can write this concentration difference as [4]

$$\Delta x_a = \frac{\Delta v}{v} \frac{2 \Delta P_L}{h\omega v_0 \pi r^2} \frac{v_L}{v_0} \quad (1)$$

Here $x_a = n_a/(n_a + n_b)$, with n_i the number density of species i , ΔP_L is the absorbed laser power, $h\omega$ is the photon energy, r is the inner radius of the LID tube, and $v_0 = \sqrt{2k_B T/m_a}$ is the thermal velocity of species a . If $\Delta v/v$ is considered independent of v_L , it follows from Eq. (1) that $\Delta x_a \propto v_L \Delta P_L$; this has the shape of a dispersion curve (see Fig. 2) since $\Delta P_L \propto \exp(-v_L^2/v_0^2)$.

Over the last decade LID has been used extensively to study the internal-state dependence of the collisional interaction for both atoms and molecules. For a review the reader is referred to Refs. 5-7.

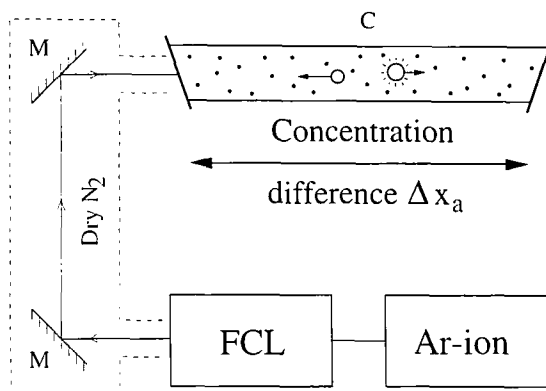


Fig. 1. Schematic diagram of the experimental arrangement. Ar-ion, argon-ion laser; FCL, color-center laser; M, plain mirror; C, LID tube. Shown is the case of laser detuning in the blue wing, i.e., H₂O molecules moving to the right are excited. For increasing cross section upon excitation, the H₂O molecules (open circles) will diffuse to the left through the buffer gas (black dots).

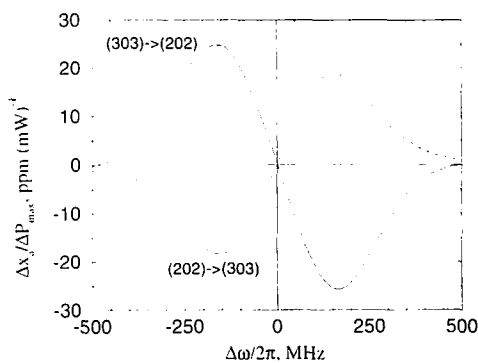


Fig. 2. Two examples of real-time LID measurements: H₂O in CH₃Cl. The concentration difference in terms of mole fraction, Δx_a , over the LID tube as a function of laser detuning $\Delta\omega/2\pi$ for the $(2, 0, 2) \leftrightarrow (3, 0, 3)$ transitions of H₂O excited in the fundamental ν_3 asymmetric stretch mode. The curves are normalized to the maximum absorbed laser power, such that the amplitude at negative detuning reflects the value of $\Delta v/v$ [cf. Eq. (1)].

2.2. Experimental Arrangement

A continuously tunable color center laser (FCL) with a single-mode output of up to 50 mW is employed for rovibrational excitation of the H_2O molecules. The wavelength region of the FCL (2.3 through 2.9 μm) completely covers the fundamental ν_3 vibrational band of H_2O and thus greatly facilitates rotational-state-selective experiments (for line positions see Ref. 8). The laser beam is sent through a (OFHC) copper capillary of length $L = 300$ mm and $r = 0.75$ mm containing the gas mixture. It typically consists of a trace of H_2O (1–10%) immersed in CH_3Cl or H_2 at a total pressure of 100 Pa and temperature $T = 295 \pm 1$ K.

In the experiment, the FCL frequency is slowly scanned through the absorption profile at a rate of ≈ 40 MHz/min, producing typical Δx_u values of 10^2 – 10^3 ppm. This is detected by means of monitoring the small variation of the heat conductivity as the composition of the gas mixture changes at either end of the tube. For this we employ a matched pair of thermistor beads in the self-heat mode (for details see Ref. 4). The absorbed laser power ΔP_L is measured by a thermopile power meter. To eliminate absorption of the laser power by atmospheric water vapor, all relevant optical components were placed under a dry N_2 atmosphere.

3. RESULTS AND ANALYSIS

The rovibrational structure of H_2O is that of an asymmetric top. All states carry labels (J, K_a, K_c) , where K_a and K_c refer to the axis of smallest and largest moment of inertia, respectively. Since for the present study the rotation of the permanent dipole moment is of interest, the measurements were limited to $(J, 0, K_c = J) \rightarrow (J \pm 1, 0, K_c = J \pm 1)$ transitions. For the rotational part of the excitation this corresponds, classically speaking, to varying the angular velocity of the in-plane rotation and, thus, of the permanent dipole moment.

Figure 2 exemplifies two results of the real-time measured concentration difference as a function of laser detuning for the $(2, 0, 2) \leftrightarrow (3, 0, 3)$ transitions of H_2O immersed in CH_3Cl . The profiles are normalized to the maximum absorbed laser power, such that their magnitudes approximately reflect $\Delta v/v$. From the difference in sign between the results for the two transitions shown in Fig. 2, it is already evident that rotation plays the dominant role in the rovibrational state-dependent intermolecular interaction, since both transitions have the vibrational excitation $v = 0 \rightarrow 1$ in common.

Since for all transitions considered the homogeneous linewidth Γ is found to be much smaller than the Doppler width kv_0 ($\Gamma/kv_0 \approx 0.03$), we can obtain $\Delta v/v$ from Δx_u using Eq. (1). For $\Delta P_L \ll P$ with P the laser power, it

is found that Δx_a is very nearly proportional to $v_L \exp(-v_L^2/v_0^2)$ such that $\Delta v/v$ only marginally depends on v_L . For the forthcoming discussion $\Delta v/v$ is considered constant for each separate transition.

Upon rovibrational (J, ν)-excitation, both the rotational and the vibrational quantum number changes. To find the separate effects of rotational and vibrational degrees of freedom on ν , we make the Ansatz that they are independent (i.e., no ν - J cross terms). If we neglect collisions that change the rotational state without randomizing the velocity, this allows us to write [9]

$$\frac{\Delta v}{v} = \left(\frac{\Delta v}{v}\right)_{\text{vib}} + \left(\frac{\Delta v}{v}\right)_{\text{rot}} \quad (2)$$

Here $(\Delta v/v)_{\text{vib}}$ and $(\Delta v/v)_{\text{rot}}$ describe the independent contributions of the change in vibrational and rotational quantum numbers to $\Delta v/v$. The individual effects of vibrational and rotational excitation can now be disentangled by combining data for $P(J)$ (i.e., $J \rightarrow J-1$) and $R(J-1)$ (i.e., $J-1 \rightarrow J$) transitions. Note that for these transitions the change in vibrational quantum number is the same ($\nu=0 \rightarrow 1$), while the change in rotational quantum number is opposite. The average and the difference of the results yield $(\Delta v/v)_{\text{vib}}$ and $(\Delta v/v)_{\text{rot}}$, respectively.

In Fig. 3, the results for $P(J)$ and $R(J-1)$ transitions are shown for both H₂O systems studied. It is seen that the average [$\equiv (\Delta v/v)_{\text{vib}}$] is independent of J for both systems to a good approximation, which experimentally confirms the validity of Eq. (2).

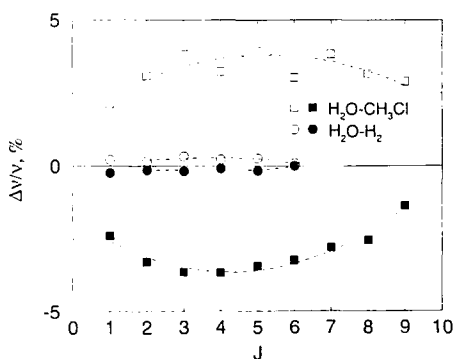


Fig. 3. The relative change in collision rate upon excitation $\Delta v/v$ as a function of rotational quantum number J for $(J, 0, J) \rightarrow (J-1, 0, J-1)$ transitions (open symbols) and $(J-1, 0, J-1) \rightarrow (J, 0, J)$ transitions (filled symbols) in H₂O-CH₃Cl and H₂O-H₂.

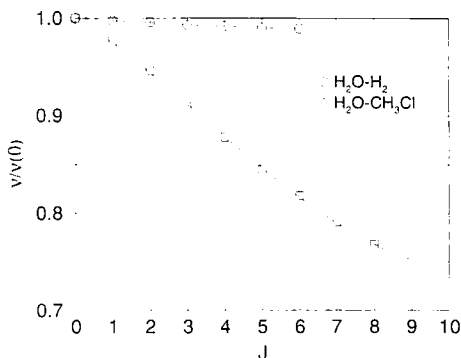


Fig. 4. The rotational-state dependence of the collision rate v for both systems. For a nonrotating H_2O molecule, v is normalized to unity.

The vibrational parts $(\Delta v/v)_{\text{vib}}$ for both systems are relatively small compared to $(\Delta v/v)_{\text{rot}}$, i.e., $(\Delta v/v)_{\text{vib}} \approx 0.20\%$ for $\text{H}_2\text{O}-\text{CH}_3\text{Cl}$ and 0.04% for $\text{H}_2\text{O}-\text{H}_2$. Since $(\Delta v/v)_{\text{rot}}$ can be considered as differentials of the transport collision rate $v(J)$ itself, it is now possible to construct the J -dependence of v by combining $(\Delta v/v)_{\text{rot}}$ for all J . The result for $v(J)$ normalized to $v(0)$ is shown in Fig. 4. It is found that v decreases by 25% if $J=0 \rightarrow 9$ for $\text{H}_2\text{O}-\text{CH}_3\text{Cl}$. In contrast, for $\text{H}_2\text{O}-\text{H}_2$ the decrease in v is only $\approx 1.0\%$ as $J=0 \rightarrow 6$.

4. DISCUSSION

The results show that the J -dependence of the interaction is much stronger than the v -dependence. A possible contribution to the J -dependence arising from optically induced angular-momentum alignment was considered in Ref. 10 and was found to be small. This was experimentally confirmed for HF in Kr and CH_3Cl . The contribution arising from alignment is therefore neglected.

The remarkably strong J -dependence of v for the $\text{H}_2\text{O}-\text{CH}_3\text{Cl}$ compared to the $\text{H}_2\text{O}-\text{H}_2$ system suggests that this arises mainly from the dipolar character of the intermolecular interaction (the permanent dipole moments of H_2O , CH_3Cl , and H_2 are 6.18, 6.23, and 0×10^{-30} C·m, respectively). A similar decrease in v for increasing J has been observed for dipolar systems involving hydrogen fluoride, e.g., for HF-HCl v drops by 20% as J_{HF} increases from 0 to 6, while for HF- H_2 v drops by only 4% [11].

An explanation of the strong J -dependence of the dipole-dipole interaction may be given in terms of a gradual change between two extreme

cases. For the limiting case of small J the rotational period is large compared to the duration of the collision. In this case the interaction is dominated by the long-range dipole-dipole potential, the *cross section* is *postaveraged* over all orientations and the average cross section will be large. For the other limiting case of large J , the period of rotation is small, the *potential* is *preaveraged* over all orientations, the dipole-dipole potential vanishes in first order and the collision cross section is small [12, 13].

Hence, the results for the dipolar H₂O-CH₃Cl system seem to corroborate the conclusion from the HF-HCl results [11] concerning a fundamental aspect of dipole-dipole interaction, i.e., the strong J -dependence of the r^{-3} potential term.

5. CONCLUSION

We have performed a systematic study of the rotational-state dependence of intermolecular interactions using light-induced drift as a tool. Measurements have been performed of the relative change in collision rate $\Delta\nu/\nu$ upon rovibrational excitation of H₂O in the fundamental ν_3 (asymmetric stretch) band with respect to CH₃Cl or H₂ as collision partner. It is found that vibrational and rotational degrees of freedom have independent effects on ν to a good approximation. For the dipole-dipole system H₂O-CH₃Cl it is found that ν drops to 75% of its nonrotating value as $J_{\text{H}_2\text{O}}$ increases from 0 to 9. This can be viewed as a result of the increased averaging-out of the dipolar interaction as the rotational quantum number increases.

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