Observation of Surface Light-Induced Drift

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(Received 1 June 1987)

In a one-component low-pressure gas, velocity-selective excitation can produce a drift due to state-dependent molecule-surface interaction. The first observation of this effect is reported for rovibrationally excited CH_3F colliding with quartz. Experiments involving different rotational sublevels within the ν_3 vibrational band indicate a strong dependence of the effect upon rotational quantum number.

PACS numbers: 34.50.Ez, 42.50.Vk, 47.45.Nd

In an atomic or molecular gas one can achieve velocity-selective excitation by tuning a narrow-band laser within the Doppler-broadened absorption profile. This gives rise to a new class of gas-kinetic effects, when there is a difference in interaction between excited- and ground-state particles with respect to their collision partner. In the case that the collision partner is a buffer-gas particle, a state-dependent collision rate gives rise to light-induced drift. This phenomenon, predicted in 1979 by Gel'mukhanov and Shalagin,[1] has been demonstrated in both atomic and molecular systems.[2] It can take spectacular forms, as shown by Werij *et al.* (optical piston,[3] optical machine gun[4]). However, state-dependent interaction can also occur in gas-wall collisions. In that case, light-induced drift should be observable in a one-component rarefied or Knudsen gas, as pointed out by Ghiner, Stockmann, and Vaksman.[5] In this Letter we report the first experimental observation of this effect, which may be called surface light-induced drift.

The principle of the experiment is illustrated in Fig. 1. A one-component gas is contained in a capillary at such low pressures that collisions with the wall dominate (Knudsen regime). A laser beam shines through the bore of the capillary (taken along the x axis) and is partially absorbed. By our tuning the laser in the Doppler-broadened absorption profile, particles are excited in a narrow velocity class around $v_{xL}=\lambda(\nu_L-\nu_0)$. Here λ and ν_L are the wavelength and the frequency of the laser light and ν_0 is the frequency of the transition. If the accommodation coefficient for transfer of parallel momentum to the wall is state dependent, the momentum transfer from the excited particles with $v_x=v_{xL}$ will not be balanced by that from their ground-state counterparts with $v_x=-v_{xL}$. Consequently, the gas will drift in the direction of the particles having the smaller accommodation. In a closed-tube configuration, this drift will result in a pressure difference $\delta p \equiv p_{\text{out}}-p_{\text{in}}$ between the two ends of the tube. In the stationary state, one finds for the relative pressure difference $\delta p/p$, in an elementary model requiring the net momentum transfer between gas and boundaries to vanish,

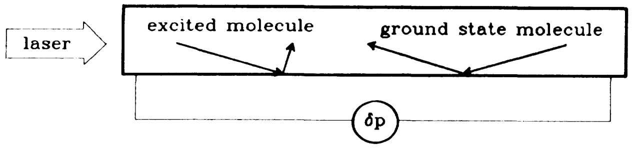

FIG. 1. The principle of surface light-induced drift measurements.

$$\frac{\delta p}{p}=-\frac{4}{\pi}\frac{n_e}{n}\frac{v_{xL}}{\bar{v}}\frac{L}{R}(\alpha_e-\alpha_g). \tag{1}$$

Here n_e/n is the fraction of excited particles in the selected velocity group around v_{xL}, $\bar{v}=(8kT/\pi m)^{1/2}$ is the mean thermal speed, L/R is the ratio of length to radius of the capillary, and $\alpha_e-\alpha_g$ is the difference in accommodation coefficients between excited and ground states. Note that the sensitivity for detection of small values of $\alpha_e-\alpha_g$ is dramatically increased by the apparatus geometry through L/R.

The experiments were performed on the symmetric-top molecule CH_3F. It has an absorption band around 9.5 μm originating from rovibrational excitation (ν_3 mode or C-F stretch). For the isotopic species $^{13}CH_3F$, the strong absorption line $R(4,3)$, i.e., $v=0\rightarrow 1$, $J=4\rightarrow 5$, $K=3\rightarrow 3$, is nearly coincident with the $9P32$ line of a CO_2 laser, the mismatch being only 26 MHz [see Fig. 2(a)]. With use of a grating-tunable cw CO_2 waveguide laser with a tuning range of 250 MHz, the full $R(4,3)$ absorption profile is easily covered since its Doppler width at room temperature is 65 MHz (FWHM). This Doppler width is under typical experimental conditions an order of magnitude larger than the homogeneous linewidth, which has contributions both from pressure broadening (0.26 MHz/Pa or 37 MHz/Torr FWHM, cf. Panfilov, Strunin, and Chapovskii[8]) and from power broadening (3 MHz cm $W^{-1/2}$, cf. Riegler *et al.*[9]).

The gas is contained in a temperature-controlled quartz capillary with dimensions $L=300$ mm and $R=0.75$ mm, yielding a value of $L/R=400$. A differential capacitance manometer with a sensitivity of 10^{-6} Torr is used to measure the pressure difference δp. Two thermopile power meters monitor the laser power

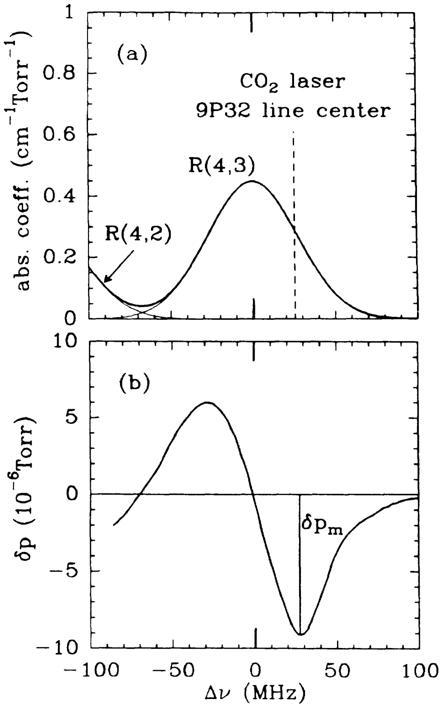

FIG. 2. (a) Doppler-broadened absorption profile of $^{13}CH_3F$ near the $9P32$ laser line. This spectrum was computed from the data given in Ref. 6; the position of the $9P32$ line was taken from Ref. 7. At the left, one notices the tail of the $R(4,2)$ line, centered at -131 MHz. (b) Typical recorder trace of the observed pressure difference vs laser detuning $\Delta\nu \propto v_{xL}$, relative to the center of the absorption line $R(4,3)$. Pressure $p = 0.030$ Torr, laser intensity $I = 5$ W/cm^2.

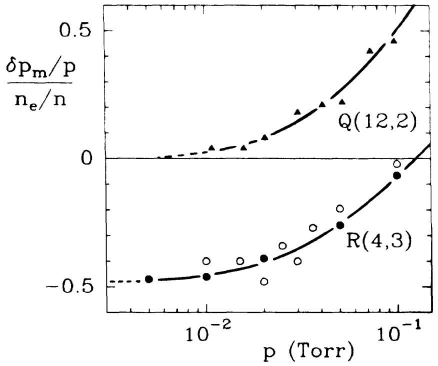

FIG. 3. Values of the maximum observed pressure difference for positive detuning [cf. Fig. 2(b)], normalized by the excited fraction, as a function of pressure, for the transitions $R(4,3)$ and $Q(12,2)$. Additional preliminary experiments for the weak absorption line $P(24,13)$ yield large positive effects (not shown). Laser intensities $I = 110$ W/cm^2 (triangles), $I = 60$ W/cm^2 (filled circles), $I = 5$ W/cm^2 (open circles).

upstream and downstream from the cell. This provides a measurement of the absorption in the gas, from which the excited-state fraction n_e/n is to be deduced (see below). A thermocouple measures the temperature difference between the two ends of the quartz capillary. This signal is used to correct for small spurious effects originating from thermal transpiration due to uneven heating of the capillary.

In the experiment, the CO_2 laser is scanned through the Doppler-broadened absorption profile, the laser power entering the cell being typically 10^{-1} to 1 W. The pressure drop along the tube as a function of the frequency detuning is recorded in real time since the response time of the system is short (≈ 12 s in the low-pressure limit). A typical result of such a scan is shown in Fig. 2(b). It is seen that the observed pressure difference is odd in detuning $\Delta\nu \propto v_{xL}$, in accordance with Eq. (1). The slight asymmetry of the signal is largely due to the neighboring $R(4,2)$ line [see Fig. 2(a)]. For a quantitative analysis of the observed pressure difference, the maximum of the effect, $\delta p_m/p$ [cf. Fig. 2(b)], is normalized by the excited fraction n_e/n. To this end, n_e is determined from the number of photons per second absorbed in the gas, which equals $\Delta P/h\nu$, with ΔP the absorbed power and $h\nu$ the photon energy. In the Knudsen limit, where all excited particles reach the wall of the tube in the selected velocity group and internal state, this number must equal the flux of excited particles, $\frac{1}{4}n_e\bar{v}$, multiplied by the capillary inner surface area (note that the radiative lifetime is long, ≈ 1 s). After straightforward substitutions, one finds

$$\frac{n_e}{n} = \frac{m\bar{v}}{4RLp\alpha_e}\frac{\Delta P}{h\nu}, \tag{2}$$

with m the particle mass. This is essentially constant throughout the tube since absorption is small (typically 1% to 10%). On the right-hand side of Eq. (2), α_e has been included to allow for molecule-wall collisions in which the particles remain in the selected velocity group around v_{xL} while preserving their excited state. Although Eq. (2) is strictly valid only in the Knudsen limit, it was used throughout since in this paper we focus on the Knudsen-limit value of the data. The value of n_e/n is found to be on the order 10^{-3} at most, because the relative population of the rotational sublevels involved is only 8×10^{-3} in thermodynamic equilibrium.

The resulting data for $(\delta p_m/p)(n_e/n)^{-1}$ vs p are given in the lower part of Fig. 3. It is seen that the effect tends to a constant value in the low-pressure limit. From this value one can, using Eq. (1), obtain the difference in accommodation coefficient for parallel momentum,

$$(\alpha_e - \alpha_g)/\alpha = +1.3\times10^{-3}, \tag{3}$$

between molecules in the vibrationally excited state $(v,J,K) = (1,5,3)$ and those in $(v,J,K) = (0,4,3)$.

In order to assess the role of the rotational levels involved, additional experiments were performed on two transitions involving different rotational sublevels. First, the $Q(12,2)$ line in $^{12}CH_3F$ was studied, which has a near coincidence with the 9P20 laser line.[8] The results are also given in Fig. 3. It is seen that the data behave markedly differently from the $R(4,3)$ case, the effect tending to zero in the low-pressure limit (the observed pressure dependence away from the Knudsen limit will be discussed in a forthcoming paper). This indicates that the difference in α between molecules in the states $(v,J,K)=(1,12,2)$ and $(0,12,2)$ is very small ($\lesssim 0.1 \times 10^{-3}$). Finally, data were obtained on the $P(24,13)$ transition in $^{13}CH_3F$, with use of the 10R30 laser line. Although absorption is weak in this case and experimental uncertainties are thus large, these data clearly show a large positive effect, opposite to that observed for the $R(4,3)$ line. Consequently, the value of α for molecules in the state $(v,J,K)=(1,23,13)$ is considerably smaller than in $(v,J,K)=(0,24,13)$.

These experiments suggest, somewhat surprisingly, that α depends only weakly on the vibrational quantum number but increases more than linearly with increasing rotational quantum number. The underlying mechanism is not yet clear. A rotational-state–dependent trapping probability seems unlikely as the major mechanism, since experimental evidence[10] on the system NO/Ge as well as physical arguments[10,11] suggest an effect with the opposite sign. The rotation-translation coupling in the direct inelastic-scattering channel may therefore be a more likely possibility.

In conclusion, these experiments provide the first measurements of surface light-induced drift. This phenomenon may be regarded as a new tool to study the internal-state–dependent molecule-wall interaction. It is very sensitive to the coupling between the incoming internal state and the outgoing trajectory. In this sense it is complementary to molecular-beam experiments, which are less sensitive to subtle changes in the average outgoing velocities. Furthermore, we conclude that for CH_3F the accommodation coefficient for parallel momentum is state dependent. These preliminary results show that it depends more strongly on the rotational than on the vibrational state of the molecule. Further experiments are in progress.

The authors wish to thank I. Kuščer, J. E. M. Haverkort, J. P. Woerdman, E. R. Eliel, G. Nienhuis, and J. J. M. Beenakker for fruitful discussions, and G. J. van der Meer for his part in the experiments. This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie, which is financially supported by the Nederlandse Organisatie voor Zuiver-Wetenschappelijk Onderzoek.

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