Method for determining the difference between the accommodation coefficients for excited and ground-state molecules in experiments with a light-induced free-molecular drift

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The accommodation coefficient in terms of the tangential momentum depends on the vibrational-rotational state of the molecule. As a result, a free-molecular drift of the gas arises in a laser beam. This drift can be exploited to determine the difference between the accommodation coefficients for the molecules at the walls of a vessel. It is shown that the conventional experimental method has a limited range of applicability and can result in large errors. The physical reason for the occurrence of errors is identified. Ways to minimize these errors are found. Requirements which would have to be met for an experimental test of the conclusions reached here are formulated.

Excited molecules (e) and ground-state molecules (g) differ in the accommodation coefficient in terms of the tangential momentum at the walls of a vessel ($\alpha_e \neq \alpha_g$). As a result, a free-molecular drift of the gas arises in a laser beam.[1,2] This drift can be exploited to determine the relative difference between accommodation coefficients.[3-5] The accommodation coefficient changes only slightly in the case of IR excitation. The drift velocity is proportional to the quantity $(\alpha_e - \alpha_g)/\alpha_g$ and is very low. Experimentally, one can measure the pressure drop[3-5] δp_0 which arises between the ends of a vessel with closed ends and which causes a free-molecular Poiseuille flow in the direction opposite the drift. There is also a direct proportionality between $(\alpha_e - \alpha_g)/\alpha_g$ and δp_0.

Since the velocity of the Poiseuille free-molecular flow is determined completely by the geometry of the vessel, the gas pressure and temperature, and the pressure drop δp_0, all that we need in order to find $(\alpha_e - \alpha_g)/\alpha_g$ is the coefficient of the proportionality between the quantity $(\alpha_e - \alpha_g)/\alpha_g$ and the velocity of the light-induced drift in a vessel with open ends. The accuracy of an experiment is determined by the sensitivity of the apparatus, the ability to measure extremely small pressure drops (pressure drops as small as 10^{-3}–10^{-4} Pa could be measured under the experimental conditions of Refs. 3–5), and the accuracy with which this proportionality coefficient is known. A novel method for determining this coefficient was proposed in Refs. 3 and 4. The following expression was derived for the drift velocity in Ref. 4 under the assumption that the absorption line has a field-broadened Voigt profile:

$$\mathbf{U}_M = -\frac{(\alpha_e-\alpha_g)}{\alpha_g}\frac{\bar{n}_e}{n} v_0 \varphi(\Omega)\frac{\mathbf{k}}{k}, \tag{1}$$

where

$$\bar{n}_e = \nu_e^{-1} n \int p(\mathbf{v})\, d\mathbf{v}, \qquad \nu_{e,g} = \alpha_{e,g} v_T/d,$$

$\nu_{e,g} = \alpha_{e,g} v_T/d$ is the average rate of Maxwellizing collisions of the molecules with the vessel walls; v_T is the average thermal velocity of the molecules; d is the diameter of the vessel; $p(v)dv$ is the probability for the excitation per unit time of molecules in the interval v, $v + dv$; $n = p_0/k_B T$; k_B is the Boltzmann constant; p_0 and T are the gas pressure and temperature; $v_0 = v_T \pi^{1/2}/2$; and $\varphi(\Omega)$ is a function introduced in Ref. 6. It is given by

$$\varphi(\Omega) = \frac{\int \mathbf{k}\mathbf{v} p(\mathbf{v})\, d\mathbf{v}}{k v_0 \int p(\mathbf{v})\, d\mathbf{v}}, \qquad p(\mathbf{v}) \sim \frac{f_M(\mathbf{v})}{\Gamma_B{}^2 + (\Omega - \mathbf{k}\mathbf{v})^2}.$$

Here k is the wave vector of the light, Ω is the detuning of the laser light from the central frequency of the transition line, $f_M(v)$ is a Maxwellian velocity distribution of the molecules, $\Gamma_B = \Gamma(1 + \varkappa)^{1/2}$, Γ is the collisional half-width of the absorption line, and $\varkappa$ is a saturation parameter.

The quantity $\bar{n}_e/n$ was determined in Refs. 3 and 4 from experimental data on the total power ΔW ($\Delta W \ll W$) absorbed over the length of the vessel, $L(L \gg d)$, from the obvious formula

$$\frac{\bar{n}_e}{n} = \frac{\Delta W}{S\hbar\omega_L L \nu_e n}, \tag{2}$$

where S is the cross-sectional area of the vessel, and ω_L is the frequency of the laser light.

Expression (1) follows from the simple model[3,4] in which the free-molecular kinetic equations with convection terms[7] are replaced by spatially uniform equations in which the boundary conditions are expressed in terms of the average rate of Maxwellizing collisions of molecules with the walls:

$$\begin{gathered} np(\mathbf{v}) - \nu_e f_e(\mathbf{v}) + \nu_e(1-\gamma) n_e f_M(\mathbf{v}) = 0, \\ -np(\mathbf{v}) - \nu_g f_g(\mathbf{v}) + (\nu_g n_g + \nu_e n_e \gamma) f_M(\mathbf{v}) = 0, \\ n_{e,g} = \int f_{e,g}(\mathbf{v})\, d\mathbf{v}, \qquad f_M(\mathbf{v}) = \frac{1}{\pi^{3/2} v_0{}^3} \exp\left(-\frac{\mathbf{v}^2}{v_0{}^2}\right). \end{gathered}$$

Here f_e and f_g are velocity distributions in the excited and ground vibrational states, and γ is the fraction of quenching collisions at the wall.

It is implicitly assumed in this model that the accommodation coefficients α_e and α_g are certain average characteristics of vibrational levels e and g, the same for each rotational sublevel, but dependent (as was shown in Refs. 3 and 4) on the particular vibrational-rotational transition $|g, J\rangle - |e, J'\rangle$ which is excited.

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In the method of Refs. 3 and 4, one can ignore the rotational relaxation of the molecules at the vessel walls (about which little is known). Without specifying the function $p(v)$, one can restrict the analysis to the equations for two vibrational levels. The model on which that method is based, however, does not contain convection terms, so it ignores the variations in the functions f_e and f_g across the vessel. It thus does not give a completely correct description of the deformation of the distribution functions. Since it is this deformation which determines the drift velocity, the accuracy of the method of Refs. 3 and 4 is not known at the outset and must be analyzed. We attempt such an analysis in the present paper.

A correct description of the drift of a molecular gas in a laser beam, which excites an individual vibrational-rotational transition $|g, J\rangle - |e, J'\rangle$, requires using the equations and the associated boundary conditions for each quantum state of the molecule. If the model of rotationally strong collisions is used for the rotational relaxation of the molecules at the wall, and if the geometry of the vessel is also simplified to a plane geometry, the equations describing this problem become

$$v_y \frac{\partial f_{ej'}}{\partial y} = np(\mathbf{v})\,\delta_{j'J'}, \tag{3}$$

$$v_y \frac{\partial f_{gj}}{\partial y} = -np(\mathbf{v})\,\delta_{jJ}, \tag{4}$$

$$f_{ej'}\left(\pm\frac{d}{2}, v_y \lessgtr 0\right) = (1-\alpha_e)\,q_{j'} f_e\left(\pm\frac{d}{2}, -v_y\right)$$

$$+(1-\gamma)\,\alpha_e n_e q_{j'} f_M(\mathbf{v}), \tag{5}$$

$$f_{gj}\left(\pm\frac{d}{2}, v_y \lessgtr 0\right) = (1-\alpha_g)\,q_j f_g\left(\pm\frac{d}{2}, -v_y\right)$$

$$+(\alpha_g n_g + \alpha_e n_e \gamma)\,q_j f_M(\mathbf{v}), \tag{6}$$

$$np(\mathbf{v}) = P_e(v_x)\,(f_{gJ} - f_{eJ'}), \qquad P_e(v_x) = \frac{2|G|^2\Gamma}{\Gamma^2 + (\Omega - kv_x)^2}.$$

Here $G = E\mu/2\hbar$, E is the electric field amplitude, μ is the matrix element of the transition dipole moment, q_j is the equilibrium fraction of the molecules which are in rotational sublevel j, and $\delta_{j'J'}$ and δ_{jJ} are Kronecker deltas.

Summing (5) and (6) over j' and j, respectively; combining the results; and noting that the function $f = f_e + f_g$ is independent of y and symmetric with respect to v_y [as follows from (3)–(4)], we easily find

$$f(v_y \lessgtr 0) = -\frac{(\alpha_e - \alpha_g)}{\alpha_g} f_e\left(\pm\frac{d}{2}, -v_y\right) + \left(\frac{\alpha_e}{\alpha_g} n_e + n_g\right) f_M(\mathbf{v}).$$

A summation of (5) over $j' \neq J'$ leads to

$$\sum_{j' \neq J'} f_{ej'}\left(\pm\frac{d}{2}, v_y \lessgtr 0\right) = (1-\alpha_e)\,(1-q_{J'})$$

$$\times\left[\sum_{j' \neq J'} f_{ej'}\left(\pm\frac{d}{2}, -v_y\right)\right.$$

$$\left. + f_{eJ'}\left(\pm\frac{d}{2}, -v_y\right)\right] + (1-\gamma)\,(1-q_{J'})\,\alpha_e n_e f_M(\mathbf{v}),$$

where, according to (3), the overall distribution function among the rotational sublevels not at resonance with the light is independent of y and is symmetric with respect to v_y. We can thus write

$$\sum_{j' \neq J'} f_{ej'}\left(\pm\frac{d}{2}, v_y \lessgtr 0\right) = \sum_{j' \neq J'} f_{ej'}\left(\pm\frac{d}{2}, -v_y\right),$$

from which we find

$$f_e\left(\pm\frac{d}{2}, -v_y\right) = \frac{f_{eJ'}\left(\pm\frac{d}{2}, -v_y\right) + (1-\gamma)\,(1-q_{J'})\,\alpha_e n_e f_M(\mathbf{v})}{1-(1-\alpha_e)\,(1-q_{J'})}$$

and

$$f(v_y \lessgtr 0) = -\frac{(\alpha_e - \alpha_g)}{\alpha_g} \frac{f_{eJ'}\left(\pm\frac{d}{2}, -v_y\right)}{1-(1-\alpha_e)\,(1-q_{J'})}$$

$$+ f_M(\mathbf{v}) \left\{\left(\frac{\alpha_e}{\alpha_g} n_e + n_g\right) - \frac{(\alpha_e - \alpha_g)}{\alpha_g} \frac{(1-\gamma)(1-q_{J'})\,\alpha_e n_e}{[1-(1-\alpha_e)\,(1-q_{J'})]}\right\}. \tag{7}$$

The accommodation coefficient α_g is usually close to one. In particular, for the interaction of $^{13}CH_3F$ molecules with a quartz surface, as in the experiments of Refs. 3 and 4, we would have $\alpha_g \simeq 0.95$. In this case the coefficients α_e and α_g can be interpreted as the accommodation coefficients of molecules in vibrational-rotational levels which are at resonance with the light.

Integrating Eqs. (3)–(4) under boundary conditions (5)–(6) for $j' = J'$ and $j = J$, we easily find, in the zeroth approximation in $(1-\alpha_e)$ and $(1-\alpha_g)$,

$$f_{eJ'}(y, v_y \gtrless 0) = \tfrac{1}{2}[n_g q_J + n_e q_{J'}(1-\gamma) + n_e q_J \gamma]$$

$$\times f_M(\mathbf{v}) - {}^1/_2[n_g q_J$$

$$-(1-\gamma)\,n_e q_{J'} + n_e q_J \gamma]\,f_M(\mathbf{v}) \exp\left[-2P_e(v_x)\left(y \pm \frac{d}{2}\right)\frac{1}{v_y}\right], \tag{8}$$

$$f_{gJ}(y, v_y \gtrless 0) = [n_g q_J + n_e q_{J'}(1-\gamma) + n_e q_J \gamma]$$

$$\times f_M(\mathbf{v}) - f_{eJ'}(y, v_y \gtrless 0). \tag{9}$$

The drift velocity is found from (7) and (8) and is given by the simple formula

$$U=\frac{(\alpha_e-\alpha_g)}{\alpha_g}\frac{\beta}{\pi}\int_{-}^{\infty}J_0[2P_e^*(V_x)]\,V_x\exp(-V_x^2)\,dV_x,$$

$$J_m(z)=\int_0^{\infty}V_y^{m}\exp\left(-V_y^2-\frac{z}{V_y}\right)dV_y,$$

$$\beta=\frac{n_gq_J-(1-\gamma)n_eq_{J'}+n_eq_J\gamma}{n}. \tag{10}$$

Here and below, all velocities are expressed in units of v_0; $V=\mathbf{v}/v_0$; and $P_e^*(V_x)=P_e(v_x)d/v_0$.

Equations (8) and (9) can be used to find the total power absorbed over the length of the vessel and thus to find $\bar{n}_e/n$. Finally, expression (2) for $\bar{n}_e/n$ becomes

$$\frac{\bar{n}_e}{n}=\frac{\beta}{2\pi^{1/2}}\int_{-\infty}^{\infty}\left\{\frac{1}{2}-J_1[2P_e^*(V_x)]\right\}\exp(-V_x^2)\,dV_x\,.$$

According to (1), the model of Refs. 3 and 4 gives the drift velocity as

$$U_M=-\frac{(\alpha_e-\alpha_g)}{\alpha_g}\frac{\beta}{2\pi^{1/2}}\varphi(\Omega)\times\int_{-\infty}^{\infty}\left\{\frac{1}{2}-J_1[2P_e^*(V_x)]\right\}\exp(-V_x^2)\,dV_x. \tag{11}$$

The pressure drop δp_0 measured under the given conditions and for the given experimental geometry determines uniquely the velocity of the Poiseuille free-molecular flow. This velocity is equal to the velocity of the light-induced drift. In general, the only way to bring the light-induced drift velocities found from Eqs. (10) and (11) into equality is to use different values of α_e. We then easily find

$$\frac{\alpha_e-\alpha_g}{\alpha_e^E-\alpha_g}=-\frac{\pi^{1/2}}{2}\varphi(\Omega)\times\frac{\int_{-\infty}^{\infty}\left\{\frac{1}{2}-J_1[2P_e^*(V_x)]\right\}\exp(-V_x^2)\,dV_x}{\int_{-\infty}^{\infty}J_0[2P_e^*(V_x)]\,V_x\exp(-V_x^2)\,dV_x}, \tag{12}$$

where α_e is the actual accommodation coefficient, and α_e^E is the accommodation coefficient found experimentally. Without any loss of generality, Eq. (12) can be extended to the case in which the light intensity varies across the cell. It can be shown that the expression $P_e(v_x)(y\pm d/2)$ in (8) is replaced by $\int_{\mp d/2}^{y}P_e(v_x)dy$, and the function $P_e^*(V_x)$ in (12) is determined by the average light intensity over the cross section.

The results of numerical calculations from (12) for a wide range of parameter values are shown in Tables I and II. Table I shows the evolution of the ratio $(\alpha_e-\alpha_g)/(\alpha_e^E-\alpha_g)$ with the light intensity; the gas pressure is constant, and we have $\Gamma/kv_0=1\cdot10^{-3}$. The calculations were carried out for $\Omega/kv_0=0.667$. The quantity $P_e^*(V_{x0})=\varkappa/\pi^{1/2}$ is the value of $P_e^*(V_x)$ at the absorption resonance. Table II corresponds to the case in which the gas pressure is varied at a constant light intensity. The detuning of the light frequency from the center of the absorption line is the same: $-\Omega/kv_0=0.667$.

Three important conclusions can be drawn from the results in Tables I and II. First, in the situations typical of the experiments the error in the determination of the difference between accommodation coefficients can exceed 100%. Second, the magnitude of the error is determined by the value of a single parameter: $-\Gamma_B/kv_0$. As Γ_B/kv_0 tends toward unity, the error in the determination of the difference between accommodation coefficients decreases. For the value $\Gamma_B/kv_0=0.941$, the equality $(\alpha_e-\alpha_g)/(\alpha_e^E-\alpha_g)=1$ holds very accurately (Table I). Several calculations were carried out with $\Gamma_B/kv_0=0.941$ and various values of Γ/kv_0 and Ω/kv_0 to see just how general this behavior is (Table III). The results show that the ratio $(\alpha_e-\alpha_g)/(\alpha_e^E-\alpha_g)$ is equal to one in all cases, with an accuracy satisfactory for the experiments. Third, since the ratio $(\alpha_e-\alpha_g)/(\alpha_e^E-\alpha_g)$ changes by an amount equal to its own value over the interval $\Gamma_B/kv_0=0.1-1$, very different values of $(\alpha_e^E-\alpha_g)/\alpha_g$ should be found as the gas pressure or the light intensity is varied over a broad range

TABLE I.

$P_e^*(V_{x0})$	Γ_B/kv_0	$(\alpha_e-\alpha_g)/(\alpha_e^E-\alpha_g)$	$P_e^*(V_{x0})$	Γ_B/kv_0	$(\alpha_e-\alpha_g)/(\alpha_e^E-\alpha_g)$
$4{,}0\cdot10^3$	0,084	0,403	$6{,}8\cdot10^4$	0,347	0,593
$1{,}0\cdot10^4$	0,133	0,444	$1{,}0\cdot10^5$	0,421	0,641
$2{,}7\cdot10^4$	0,220	0,508	$5{,}0\cdot10^5$	0,941	1,002
$3{,}4\cdot10^4$	0,245	0,526	$1{,}0\cdot10^6$	1,331	1.365
$5{,}0\cdot10^4$	0,298	0,561			

TABLE II.

Γ/kv_0	Γ_B/kv_0	$(\alpha_e-\alpha_g)/(\alpha_e^E-\alpha_g)$
$1{,}5\cdot10^{-4}$	0,133	0,444
$2{,}0\cdot10^{-4}$	0,155	0,461
$4{,}0\cdot10^{-4}$	0,220	0,508
$5{,}0\cdot10^{-4}$	0,245	0,526
$1{,}0\cdot10^{-3}$	0,347	0,593

TABLE III.

Γ/kv_0	Ω/kv_0	$(\alpha_e-\alpha_g)/(\alpha_e^E-\alpha_g)$
$1\cdot10^{-4}$	0,250	1,076
$1\cdot10^{-3}$	0,250	1,074
$1\cdot10^{-4}$	0,667	1,002
$1\cdot10^{-3}$	0,667	1,002
$1\cdot10^{-2}$	0,667	1,007
$1\cdot10^{-4}$	1,000	0,914
$1\cdot10^{-3}$	1,000	0,914

corresponding to this interval of Γ_B/kv_0 values. An experiment formulated in this manner would double as a check of the method of Refs. 3 and 4 and as a check of the conclusions of the present paper regarding the role of the convection terms. If the effect predicted above is indeed seen, one can assume that this analysis represents the method of Refs. 3 and 4 correctly. One can also suggest that the error of the method is indeed at a minimum under the condition $\Gamma_B/kv_0 \approx 1$ and that one should attempt to satisfy this condition in planning experiments. For molecules with closely spaced rotational levels, it may be difficult to adhere to this recommendation, because nearby lines would come into play in the absorption.

In the experiments of Refs. 3 and 4, Γ_B/kv_0 was varied over a narrow interval of values. Although there is an error of 70–100% in the determination of $(\alpha_e - \alpha_g)/\alpha_g$, it cannot be seen. In the interval $\Gamma_B/kv_0 = 0.22 - 0.35$ [the $0 \to 1$ transition of the ν_3 mode, the $R(4,3)$ line of the $^{13}CH_3F$ molecule; excitation by the $9P(32)$ line of a CO_2 laser; $\Omega/kv_0 = 0.667$], the ratio $(\alpha_e - \alpha_g)/(\alpha_e^E - \alpha_g)$ varies by less than 15%. If we incorporate in (2), along with ν_e, the finite collision rate which prevails in a gas under actual experimental conditions (as in Ref. 4), the ratio $(\alpha_e - \alpha_g)/(\alpha_e^E - \alpha_g)$ remains essentially constant over the entire pressure range, and the error is not seen. Measurements carried out at $\Gamma_B/kv_0 \lesssim 0.1$ were also reported in Ref. 3. Unfortunately, those results were obtained at the limit of the capabilities of the measurement apparatus, and they cannot be used for comparison because of their large error.

One might suggest that the reason for the increase in the experimental error with decreasing $\Gamma_B/kv_0 < 1$ is as follows. Under the condition $\Gamma_B/kv_0 < 1$, the only molecules which can be excited are those which traverse the distance d between the walls of the vessel at a low velocity v_y. There is an increase in the relative contribution to the drift velocity of molecules for which the condition $v_y < v_T$ holds. In this case the effective rate of Maxwellizing collisions is lower than the rate $\nu_e \approx v_T/d$ in the model of Refs. 3 and 4. It follows from (1) and from the definition of $\bar{n}_e$ that the use of a higher rate ν_e (higher than the effective rate) would have the consequence that the difference between accommodation coefficients found from the experimental data would be exaggerated.

In an experiment in which the geometric parameters of the vessel are fixed, it is difficult to vary the gas pressure over a wide range. A lower limit is set on the pressure by the sensitivity of the pressure gauge, since under otherwise equal conditions the pressure drop δp_0 which can be measured experimentally decreases with decreasing gas pressure. The maximum permissible gas pressure is set by the condition $\Delta W \ll W$, which is imposed by the method of Refs. 3 and 4. Since the absorbed power increases with increasing pressure, while the minimum measurable value of ΔW is fixed and depends on only the capabilities of the measurement apparatus, there is an upper limit on the gas pressure. These difficulties can be overcome by raising the sensitivity of the apparatus or by carrying out experiments in vessels of various lengths, so that ΔW can be maintained within the given range.

Since the conditions for free-molecular drift must be satisfied in order to keep the experiments "clean," yet another upper limit is imposed on the gas pressure. In particular, despite the fact that the region of the lowest pressures in the experiments of Refs. 3 and 4 corresponded to Knudsen numbers Kn = 4–2, and collisions in the gas were fairly infrequent, the drift conditions were not free-molecular conditions. This point can be understood easily by noting that the extent to which a gas is rarefied is determined in this case by the effective rate at which molecules collide with the walls, divided by the collision rate in the gas. Since the effective rate under the experimental conditions of Refs. 3 and 4 was much lower than the average rate, the effective Knudsen number was approximately one, and it would be incorrect to determine the difference between accommodation coefficients from the free-molecular formulas. Experiments with vessels of various diameters provide an additional possibility for controlling the extent to which the gas is rarefied and for expanding the range of pressures which can be used.

Over the interval $\Gamma_B/kv_0 = 0.1–1$, the drift velocity is on the order of the drift velocity in the experiments of Refs. 3 and 4, and there are no fundamental difficulties in varying the light intensity over a wide range.

Finally, we should point out that a general requirement on the gas pressures and light intensities is set by the inequality $\delta p_0 \gg p_L = \Delta W/Sc$, where p_L is the radiation pressure, and c is the velocity of light. This inequality was satisfied by a wide margin in the experiments for Refs. 3 and 4.

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