Preliminary measurements illustrating the effect of desorption and molecular residence times on the molecular drag process

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In this article we describe preliminary experiments based on a technique originally devised by Holst and Clausing [G. Holst and P. Clausing, Physica (The Hague) **6**, 48 (1926)] whereby molecules are beamed onto a disk rotating at high speed and the point of desorption identified. This in principle provides a means for the direct determination of molecular residence times. Preliminary results indicate that the residence times of helium, nitrogen, oxygen, krypton, xenon and Suva (a refrigerant) on oxidized aluminum are not in the range of 0.1 ms–1 s. An experimental facet possibly indicating a residence time for carbon dioxide on oxidized aluminum at 27 °C of 0.62 ms was identified. The possible application of the technique to gas separation is also discussed. © *1999 American Vacuum Society.* [S0734-2101(99)07404-7]

I. INTRODUCTION

Knowledge of the molecular residence time τ is a fundamental factor in the understanding of molecule-surface interactions and has special relevance in the analysis of the molecular drag process and mechanisms which exploit this phenomenon. τ is dependent on the strength and nature of the bond formed between the adsorbed molecule and the surface; it varies according to gas species, surface type and condition and temperature. The residence time (in seconds) can be described by the Frenkel equation

$$\tau=\tau_0 \exp\left(\frac{E_B}{RT}\right), \tag{1}$$

where E_B is the binding energy (in J/mol), R is the universal gas constant, T is the thermodynamic temperature and τ_0 is a constant. The definitive derivation and interpretation of this equation were developed by de Boer.[1] τ_0 is generally interpreted as the vibrational period of the adsorbed molecules; this is the case for ''supermobile adsorption'' (freely translating and rotating adsorbed molecules), and here a value of $\tau_0=10^{-13}$ s is often used. Experimentally, however, values of the pre-exponential factor have been found[2–7] to lie in the range of $10^{-4}-10^{-16}$ s. This is consistent with the occurrence of other possible circumstances of adsorption under equilibrium conditions.

II. PRINCIPLE

A variety of techniques such as molecular streaming through capillaries[3,5] and stimulated desorption methods[6,7] has been exploited to measure the residence time directly. The experimental configuration discussed in this article exploits the simplicity of the technique first described by Holst and Clausing[4] in 1926. Technical limitations meant that Holst and Clausing were only able to establish limits to the value of the residence time of Cd molecules on various surfaces. The general principle of the technique developed is shown schematically in Fig. 1. The point of adsorption of molecules onto a rotating disk is controlled via a gas injection needle and the point of desorption (describable by the Knudsen cosine law) is identified via a gas sampling needle (Holst and Clausing ''froze'' desorbing molecules onto a plate). With known disk frequency f, the measured angular shift ϕ in radians, between the point of adsorption and the point of desorption, gives a measure of the residence time. Assuming the gas desorbed in the first rotation, the measured value of $\tau=(2\pi f)^{-1}\phi$. A correction is needed to account for the effect of the bias velocity v_b developed by the disk. In the laboratory frame of reference, molecules leave the surface of the disk according to the Knudsen cosine law, but with the additional tangential bias velocity superimposed due to the rotation of the disk (molecules desorb on average perpendicular to the disk's surface at a mean thermal velocity applicable for the gas under consideration). The theory assumes a constant rate of desorption. For the experimental conditions described below $0\leq v_b\leq 239$ ms^{-1} which is to be compared to the mean thermal velocities 476 ms^{-1} for N_2, 1260 ms^{-1} for He and 220 ms^{-1} for Xe at 27 °C. Hence in the time taken for the (N_2) molecules to travel between the disk and the sampling needle they travel forward by <2 mm compared with the circumference of operation of 239 mm.

In our new application of this method the sampling needle is held perpendicularly above the surface of the disk and connected to a residual gas analyzer which measures the detected signal of the gas under test. The detected signal of the test gas is monitored as a function of disk frequency. The developed flow of test gas through the in needle will cause a

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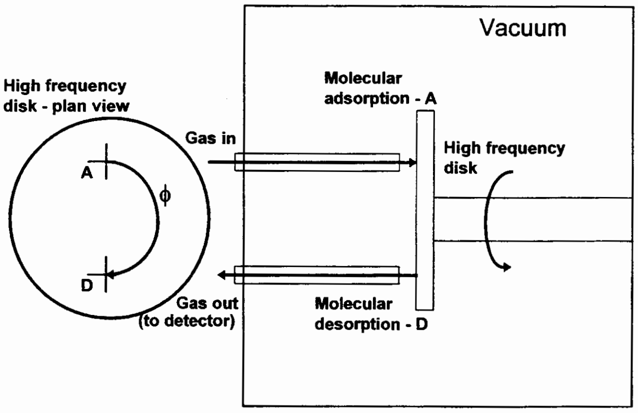

FIG. 1. Principle of the method of measurement of residence times.

rise in the measured background signal of that gas. Hence, if the point of desorption is in line with the sampling needle, the measured signal would be expected to show a peak above the background. Equation (1) can be transformed as

$$\ln(\tau)=\frac{E_B}{R}\frac{1}{T}+\ln(\tau_0). \tag{2}$$

Assuming that the binding energy and the pre-exponential factor are temperature independent, a plot of $\ln(\tau)$ vs $1/T$ would allow the binding energy and pre-exponential factor to be determined.

III. EXPERIMENT

Figure 2 shows a schematic of the experimental configuration. A BOC Edwards EXT250M turbomolecular pump was adapted to accommodate an aluminum disk (of 92 mm radius). This served as the high speed disk and was driven at variable frequencies from 0 to 1000 Hz, as measured by a tachometer. A manipulator was used to set the position of the "in" (gas injection) and "out" (gas sampling) needles. This apparatus was housed in a turbomolecular pumped ultrahigh vacuum (UHV) stainless steel chamber with typical base pressure of below 10^{-7} mbar. The out needle was connected to a Hiden Analytical HAL II quadrupole residual gas analyzer, itself housed in a separate UHV system (with base pressure 5×10^{-10} mbar). It was used to measure relative changes in the detected signal; changes lower than 0.5% being achievable with careful measurements. The in and out needles, 0.7 mm in diameter and 1 cm long, are connected to flexible pipes 4 mm in diameter and 62 cm long. A differential valving mechanism allows these pipes to be evacuated directly via the main chamber. The gas inlet and outlet pipework are such as to separate the introduced gas from the test chamber except via the in and out needles. The in and out needles were both held at a fixed radial position of 38.0 ± 0.1 mm and a fixed disk-needle height of 4 mm. The azimuthal angular position ϕ between the two needles (ϕ increasing in the direction of disk rotation) and disk-needle heights were variables for the out needle. The experimental measurement range for τ is 1 s–1 μs. The in needle is positioned at a fixed angular position with the radial and disk-needle height able to be varied. Since the residual atmosphere saturates the disk surface within seconds, molecule-molecule bonds must be considered. The problem of the flow of a gas under pressure from a nozzle (i.e., the in needle) into a high vacuum chamber has been extensively studied.[8,9] The jet profile is in most cases either a Gaussian or a Lorentzian function in cross section. The gas flow through the inlet pipe was calculated to be turbulent choked flow.

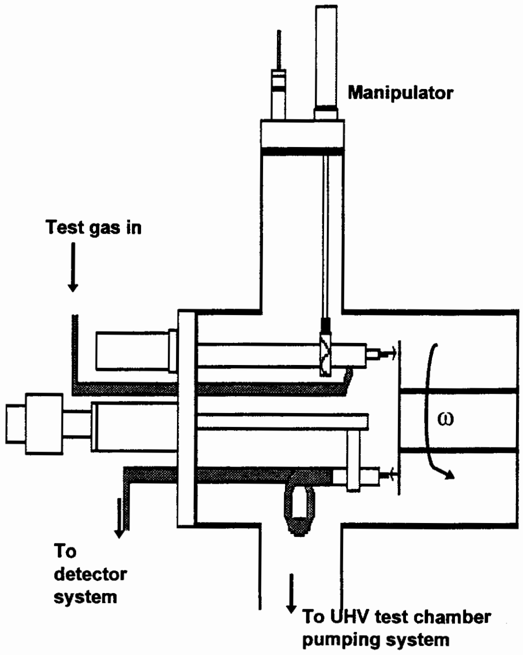

FIG. 2. Schematic of the experimental configuration.

The experimental procedure was as follows. A variety of gases (He, N_2, O_2, CO_2, Kr, Xe and Suva HFC-134a, a refrigerant gas $C_2H_2F_4$) was introduced in turn onto the aluminum disk, with the test chamber pressure rising to the 10^{-4} mbar range. Under these circumstances the detector tube has a transmission probability (for N_2) of 0.12 and an operational throughput of approximately $5\cdot10^{-7}$ mbar l s^{-1}. The base pressure was recovered between each experiment. The detected signal from the out needle was measured as a function of disk frequency. As discussed earlier the presence of a peak would indicate the position of desorption and hence facilitate a determination of the residence time. In some experiments the azimuthal position of the out needle was varied. Thermal equilibrium and stable pressures were maintained throughout; it takes several minutes to gain a new system equilibrium. The operating temperature was 27 °C unless otherwise stated.

IV. RESULTS AND DISCUSSION

Figure 3 shows typical results for He and CO_2, where the detected signal at a given disk frequency relative to that at zero frequency is plotted against disk frequency. With the exception of a peak in the CO_2 signal (consistently seen between 800 and 940 Hz and discussed below) the detected signals fall off almost linearly. This was also the case for N_2,

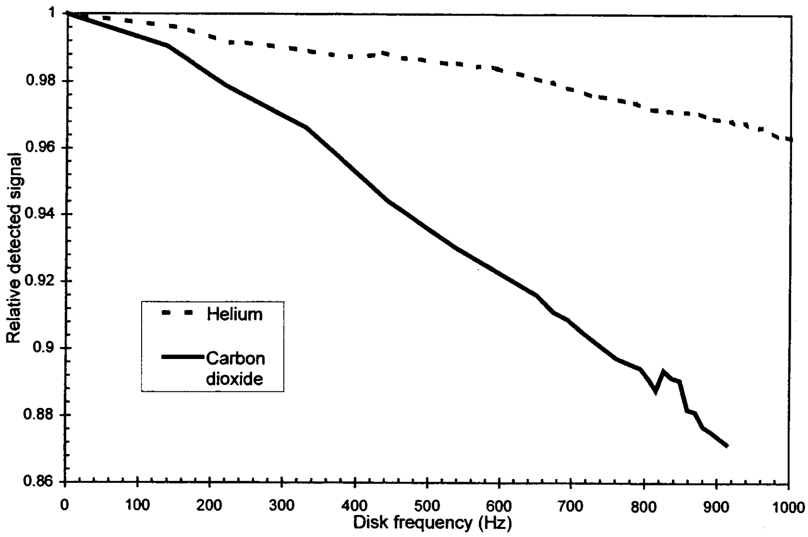

FIG. 3. Relative drop of the He and CO_2 detected signal vs disk frequency.

O_2, Kr, Suva and Xe, where no peak akin to that of CO_2 was seen. The absence of a peak indicates that for the combinations of He, N_2, O_2, Kr, Xe and Suva on (gas) on oxidized aluminum the residence time at 27 °C does not lie in the range of 0.1 ms–1 s (technical limitations prevented the achievement of the theoretical measurement limit into the μs range).

Figure 4 shows the drop in detected signal (from that at 0 to that at 1000 Hz) for the seven gases, and normalized to the drop for N_2 versus relative molecular mass. The error bars incorporate uncertainties calculated from the spread of data in repeated measurements. The dashed line represents the theoretical drop, normalized to N_2, plotted against the square root of the relative molecular mass. This theoretical curve is determined from a first principles consideration of the molecular drag phenomenon whereby the magnitude of the molecular drag effect[10] (under molecular flow conditions) is proportional to $(m/T)^{1/2}$, where m is the molecular mass. As discussed earlier, this effect manifests itself in the imposition of a bias velocity, tangential to the radial motion, on the adsorbed molecules. This is more significant (relative to the mean thermal velocities) for higher molecular mass gases. The Knudsen cosine distribution is effectively skewed in the direction of rotation in the laboratory frame. As the frequency increases, the skewing of the distribution becomes more pronounced, fewer molecules desorb perpendicularly (and directly into the out needle) from the surface of the disk and the detected signal is expected to drop. The nearly linear fall shown in Fig. 3 (and seen for other gases) is consistent with the linear increase of the bias velocity with rotational frequency. With the exception of O_2, the data fit the theoretical curve in Fig. 4 remarkably well. The seemingly aberrant behavior of O_2 needs further investigation but is at this stage attributed to the limited data set available for this gas. These results show the differential effect of molecular drag as a function of molecular mass.

To further investigate the drag phenomenon He:CO_2 and He:Xe gas mixtures were introduced into the chamber, the original ratios being approximately 50:50. Since the drop in the detected signal is larger for molecules of higher molecular mass, a relative rise of He in the composition of the gas mixtures is expected as the disk frequency increases. Table I

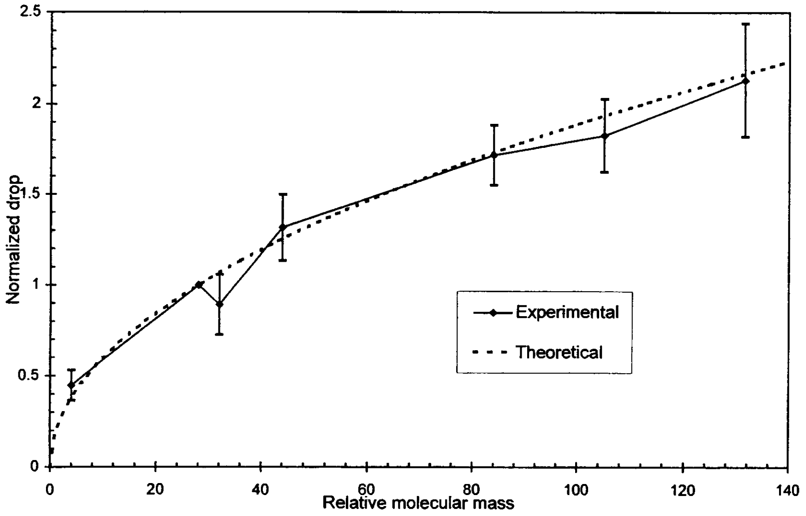

FIG. 4. Drop normalized to that of N_2 vs relative molecular mass for a range of gases.

TABLE I. Change in proportion of helium in different gas mixtures at a high disk frequency.

Gas mixture	Disk frequency ±0.1 Hz	Rise in He composition of gas mixture
He:Xe	0.0	0.0%
He:Xe	480.7	2.9%±0.3%
He:CO_2	0.0	0.0%
He:CO_2	480.7	1.8%±0.2%

shows the observed rise in He in the He:CO_2 and the He:Xe gas mixtures. Note that only relative changes in the detected signal are considered and the absolute proportions of the gases in the mixtures are unimportant, assuming that they remain constant throughout the measurements. The rise in helium in the He:Xe mixture compared to that in the He:CO_2 would be expected to be a factor of $(m_{Xe}/m_{CO_2})^{1/2} = (131.3/44)^{1/2} = 1.7$. The experimentally determined factor was $2.9/1.8 = 1.6 \pm 0.2$. This result again is consistent with the drag effect being proportional to the square root of the molecular mass and extends to gas mixtures. However, a cautionary note must be sounded concerning the He:Xe gas mixture. Mixing of Xe and He at atmospheric pressure may lead to the clustering of Xe molecules when they expand into vacuum. This effect, although not indicated by the results, needs further consideration. It is possible to consider the change in concentration of gas mixtures as the basis of a gas separating device.

Figure 5 shows the detected signal of CO_2 as a function of disk frequency in a variety of situations for different angular positions of the out needle and at different temperatures. In all cases, a peak was consistently observed in the relative detected signal between 800 and 940 Hz, but no such peak was observed for any of the other gases investigated. The finite width of the peaks (approximately 40 Hz) is consistent with a three dimensional cosine distribution of desorption velocities. At the position of the peak there are two contributions to the detected signal, the relative fall with increasing disk frequency and the addition to the signal at the point of desorption. The relative nature of the former precludes an estimate of the expected peak magnitude. It is tentatively proposed that the consistently observed peak indicates a position of desorption and hence the residence time of CO_2 molecules (on CO_2 molecules) on oxidized polycrystalline aluminum. Since only one peak was observed, it can be assumed that the molecules desorb during the first rotation. If the peak is indeed due to the residence time, then at higher φ, the peak is expected to move to higher frequencies. This is the case shown in Fig. 5. From Eq. (1) it can be seen that at higher temperatures the residence time is expected to decrease exponentially; hence with φ fixed, the frequency corresponding to the peak is expected to increase with temperature. This was the case measured for the data at 37 °C. Note that there is an expected (lower) change in the effect of drag at the higher temperature but this does not explain any frequency pinpointing of the peak. The mean of all the CO_2 data gives $\tau = 0.62 \pm 0.03$ ms at 27 °C; this includes a correction for the bias velocity discussed earlier. No values have been found in the literature for CO_2 on polycrystalline or oxidized aluminum.

V. CONCLUSIONS

The method originally developed to measure residence times has enabled a means for the determination of the differential drag effect for gases of different molecular mass and the results obtained are consistent with theory. The effect is also observed in gas mixtures and provides a possible method for gas separation. Like in a gas centrifuge, the gas mixture could be repeatedly passed through the system until the desired gas composition was reached. Certain effects relating to the possible clustering of xenon molecules and any surface effect through a gas layer need further investigation. The results indicate that the residence times of gas molecules of He, N_2, O_2, Kr, Suva and Xe on (molecules) on oxidized

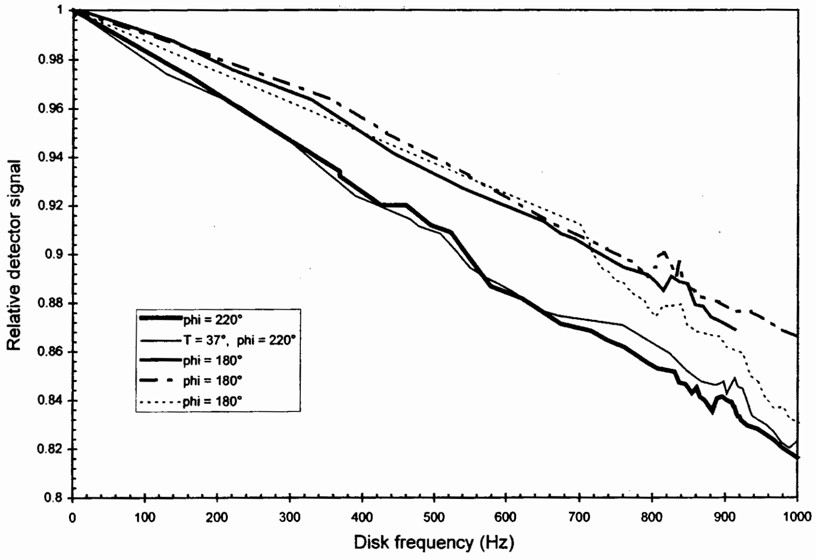

FIG. 5. Repeated measurements of the relative drop of the CO_2 detected signal vs disk frequency.

aluminum are not in the range of 0.1 ms–1 s. If the peak consistently seen for CO_2 corresponds to the point of desorption of the molecule then this indicates a residence time of 0.62 ms for CO_2 on oxidized aluminum at 27 °C. Further experiments are required especially with other gases of equivalent molecular mass to that of CO_2 but different chemistry, for example, nitrous oxide (N_2O) or propane (C_3H_8). Any residence time peak could potentially be exploited in a refinement of the gas separation technique outlined above. Providing the gas species in a mixture had peaks at widely different frequencies, it would be possible to "tune" into one peak to obtain an enriched gas mixture. By repeating this process, the desired gas composition could be obtained. Further experiments are planned at lower aluminum disk temperatures and/or higher disk frequencies which will bring (expected) residence times of many gas/surface combinations into the experimental measurement range.

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