N.

CONF-780728--3

Presented at the XIth International Symposium on Rarefied Gas Dynamics, Cannes, France, July 3-8, 1978

LBL-7395

INTERNAL ENERGY DEPENDENCE OF MOLECULAR CONDENSATION COEFFICIENTS DETERMINED FROM MOLECULAR BEAM SURFACE SCATTERING EXPERIMENTS

Steven J. Sibener and Yuan T. Lee

May 1978

Prepared for the U. S. Department of Energy under Contract W-7405-ENG-48

MASTER

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

INTERNAL ENERGY DEPENDENCE OF MOLECULAR CONDENSATION COEFFICIENTS DETERMINED FROM MOLECULAR BEAM SURFACE SCATTERING EXPERIMENTS

Steven J. Sibener and Yuan T. Lee

Materials and Molecular Research Division
Lawrence Berkeley Laboratory and
Department of Chemistry
University of California, Berkeley, CA 94720 USA

ABSTRACT

An experiment has been performed which confirms the existence of an internal mode dependence of molecular sticking probabilities for collisions of molecules with a cold surface. The scattering of a velocity selected effusive beam of CCl_4 from a 90 K CCl_4 ice surface has been studied at five translational velocities and for two different internal temperatures. At a surface temperature of 90 K (~99% sticking probability) a four fold increase in reflected intensity was observed for the internally excited (560 K) CCl_4 relative to the room temperature (298 K) CCl_4 at a translational velocity of 2.5×10^4 cm/sec. For a surface temperature of 90 K all angular distributions were found to peak 15° superspecularly independent of incident velocity.

I. INTRODUCTION

The dynamics of gas-surface interactions can be studied in detail with molecular beam surface scattering techniques.[1] For example, data on surface residence times of trapped molecules, as well as velocity and angular distributions of scattered molecules, can all be obtained from beam-surface scattering experiments. With this information some very important questions relating to gas-surface interactions, such as gas-surface energy transfer, can be explored. At this time our main intent is to investigate whether, and to what extent, sticking probabilities for collisions of molecules with a cold surface depend upon the *internal* energy of the incident molecules. Recently, both theoretical[2] and experimental[3,4] investigations of this internal energy dependence have appeared in the literature. However, bulk kinetic experiments, such as those performed by the Russian groups, can not probe the detailed dynamics of the condensation process. Also, the internal energy effect reported in the laser excited BCl_3 experiment[4] has thus far not been observed in an attempted reproduction of that experiment.[5] In this paper an experiment will be described that directly confirms the existence of an internal energy dependence of molecular sticking probabilities for collisions of molecules with a cold surface. Specifically, this internal energy dependence as a function of incident velocity is reported for CCl_4 molecules scattering from a CCl_4 ice surface. This may eventually be of interest not only to scientists in the field of surface dynamics, but also to researchers investigating new methods of heterogeneous laser isotope separation.

II. EXPERIMENT

For this experiment our universal molecular beam machine[6] was modified to include a liquid nitrogen cooled target surface. The underlying target substrate of polycrystalline copper was prepared in a procedure similar to that described by Ahearn et al.[7] At a surface temperature T_S = 280 K the copper surface was undoubtedly contaminated with many molecular species (background pressure ~10^{-7} torr), but at the experimental target temperature of 90 K - where the sticking probability of CCl_4 was found to be greater than 99% - a relatively "clean" surface of solid CCl_4 was presented to the incident molecular beam due to constant CCl_4 deposition. Figure 1 is an assembly diagram showing the important experimental components. The effusive, heated, and velocity selected beam source constructed for this experiment permits the independent variation of T_B and v_B, the beam temperature and beam velocity, respectively. This permits the study of gas-surface collisions with CCl_4 molecules having different internal energies (i.e., beam temperatures) but the same translational energies. The beam temperatures used were 298 K and 560 K, while five translational velocities in the range 2.5×10^4 cm/sec to 5.1×10^4 cm/sec were used. The target surface was cooled with liquid nitrogen and had an ultimate temperature T_S = 90 K. Nichrome wire heaters embedded in the surface support block permitted operation at temperatures above 90 K. The surface temperature was monitored with two calibrated iron-constantan thermocouples. The incident beam-surface angle θ_i is variable and was fixed at 50° measured from the surface normal. Alignment of the surface was accomplished by reflecting a HeNe laser from the surface and noting both the laser beam-surface intersection point and the angle of specularly reflected light. The reflected CCl_4 molecules were detected by an electron bombardment ionizer/quadrupole mass spectrometer assembly which has been previously described in detail.[6] The detector rotates about the surface allowing angular scattering distributions to be obtained for reflected angles $\theta_r = 30° \rightarrow 90°$. Only in-plane scattering was detected in these experiments with the plane determined by the surface normal and the incident beam. Time-of-flight (TOF) velocity distributions have also been obtained for scattering done at temperatures above the condensation point of CCl_4 using single shot techniques. Future studies will employ cross-correlation[8] TOF technqiues to obtain velocity distributions of scattered molecules below the condensation point.

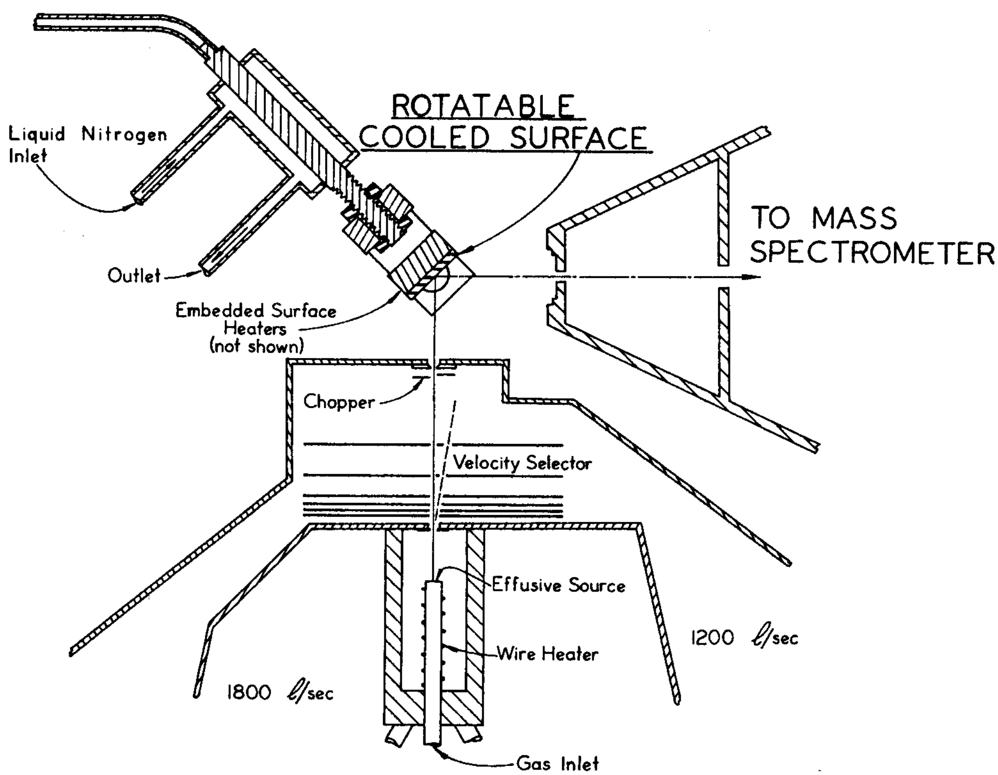

Fig. 1. Assembly diagram of the experimental scattering configuration.

This experiment was performed at T_S = 90 K (~99% sticking probability) in an attempt to distinguish inelastic collisions from adsorptions followed by subsequent reevaporation. This is accomplished by taking note of the following: at T_S = 90 K the residence times of adsorbed (trapped) molecules are significantly greater than 1 ms while the residence times of inelastically scattered CCl_4 molecules are several orders of magnitude less than 1 ms. Thus, by gating the counting electronics with a 150 Hz tuning fork chopper (Fig. 1) the short residence time CCl_4 molecules (relative to ~1 ms) can be distinguished from the trapped molecules.

III. RESULTS

Angular distributions have been obtained for CCl_4 scattering as a function of incident velocity, internal energy, and surface temperature. All angular distributions measured for surface temperatures above the beam condensation temperature of 142 K are found to be cosine with respect to the surface normal. Figure 2 shows the experimental angular distribution which was found for all incident beam conditions with T_S = 280 K. This cosine scattering pattern indicates virtually

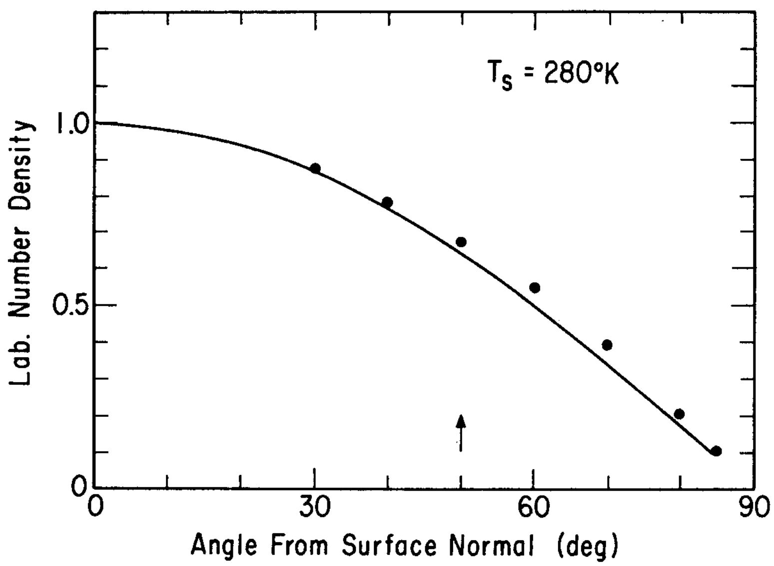

Fig. 2. T_S = 280 K experimental scattering distributions for translational energies between 2.5 x 10^4 cm/sec and 5 x 10^4 cm/sec at beam temperatures of 298 K and 560 K are all described by the solid dots (•). The solid line is a plot of the cosine (θ) function.

complete CCl_4 translational energy accommodation with the surface - a conclusion verified with subsequent time-of-flight measurements. We therefore observe that the scattered molecules come off the surface with a velocity corresponding to T_S = 280 K regardless of their incident internal or translational energies.

The angular distributions taken below the condensation temperature of the CCl_4 beam exhibit a marked difference from those discussed above. The distributions are fairly broad and peak superspecularly 15° from the specular angle of 50°. Figure

3 shows the angular distributions for collisions with T_S = 90 K and T_B = 560 K at six different incident velocities.

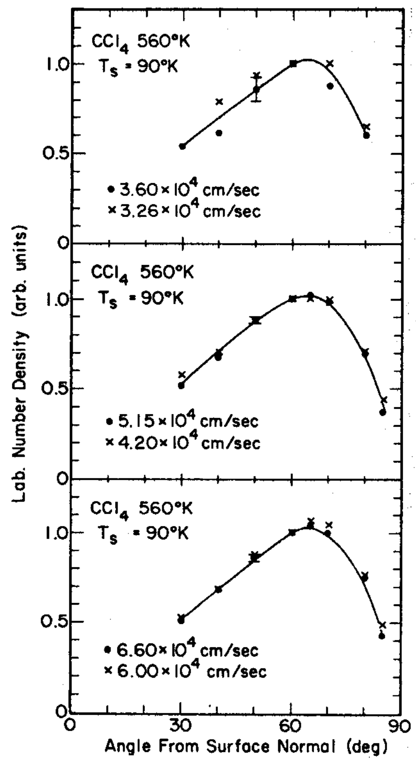

Fig. 3. Scattering distributions obtained with T_S = 90 K for six translational velocities with T_B = 560 K. The peaks all fall approximately 15° from the specular angle of 50°.

We note that, on the average, CCl_4 molecules appear to experience constant relative momentum loss collisions with the surface. We infer this from the lack of peak scattering angle variation as a function of incident velocity. Future TOF studies will directly test the validity of this inference. Figure 4 shows the T_S = 90 K and T_B = 298 K angular distributions. These also peak 15° from the specular angle and may be somewhat narrower than the hot beam distributions. However, the lower signal intensities observed here, relative to the T_B = 560 K scans, produce a much greater uncertainty in the observed shapes of the distributions. Although not shown here, all distributions are observed to become more cosine shaped when

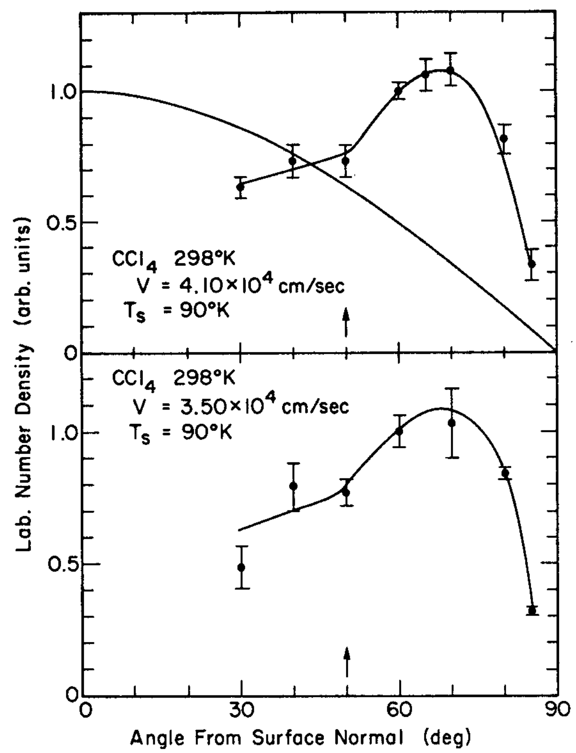

Fig. 4. Scattering distributions obtained with T_S = 90 K for two translational velocities with T_B = 298 K. Cosine(θ) is also plotted in the upper graph.

these measurements are made at ~90% sticking probability - indicating that a higher percentage of accommodated scattering is contributing to our observed signal. This observation supports our decision to conduct these studies at T_S = 90 K where the accommodated (trapped) molecules are preferentially removed relative to inelastic collisions.

If we assume, as in a hard-cube model,[9] that the tangential velocity of the CCl_4 is conserved during the collision, then we can infer approximate energy accommodation coefficients, α_E, from the angular distributions shown in Figs. 3 and 4. In fact, the α_E values obtained in this manner can only serve as <u>lower bound estimates</u> for the true α_E values in which tangential momentum loss almost certainly occurs. Note that α_E is defined as

$$\alpha_E = \frac{E_i - E_r}{E_i - E_s} \tag{1}$$

where E_i is the incident beam translational energy, E_r is the reflected beam translational energy, and E_s is the translational energy of a molecule at T_S. Within this framework α_E is found to be ~0.37 for $v_i = 2.5 \times 10^4$ cm/sec and ~0.30 for $v_i = 5.0 \times 10^4$ cm/sec. These values correspond to a 45% relative momentum loss in the momentum component perpendicular to the surface.

Finally, we have determined the internal energy dependence of CCl_4 sticking probability and have expressed this in the form of an enhancement factor, EF, which is the ratio of relative reflected fluxes for molecules having the same translational velocity, v_i, but different internal energies due to different beam temperatures:

$$EF(T_S = 90\text{ K}, v_i) = \frac{(\text{Fraction of flux reflected; } T_B = 560\text{ K})}{(\text{Fraction of flux reflected; } T_B = 298\text{ K})}$$

$$= \frac{\left.\left(\dfrac{n_r^{90}\, v_r^{90}}{\text{Incident flux } (T_B;\, v_i)}\right)\right|_{T_B = 560\text{ K}}}{\left.\left(\dfrac{n_r^{90}\, v_r^{90}}{\text{Incident flux } (T_B;\, v_i)}\right)\right|_{T_B = 298\text{ K}}}$$

where n_r^{90} and v_r^{90} are the reflected number densities and velocities at $T_S = 90$ K for each beam temperature. Figure 5 shows the EF values determined for five incident velocities between 2.5×10^4 cm/sec and 5.0×10^4 cm/sec. An enhancement factor of about 4 was observed for the slowest velocity studied. This implies that internally excited CCl_4 molecules with $v_i = 2.5 \times 10^4$ cm/sec are four times more likely to scatter from the surface than vibrationally cold molecules. Note that the actual v_r^{90} values which appear in the expression for EF were not experimentally determined here, and that the values shown in Fig. 5 were calculated assuming equal reflected velocities for scattered molecules which had the same incident velocities but differing internal energies. In reality, the scattered molecules which were initially internally excited may scatter with larger reflected velocities. The EF values of Fig. 5 may therefore be viewed as lower bound estimates for enhanced scattering due to internal excitation.

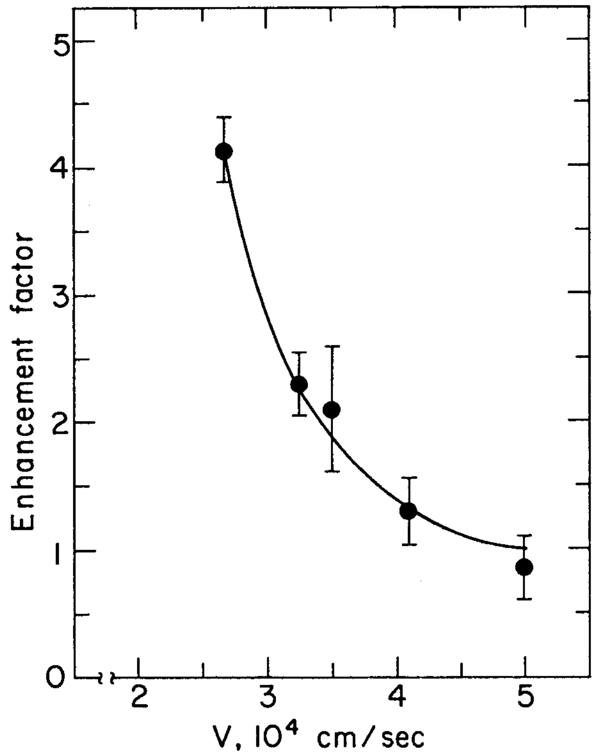

Fig. 5. Internal energy desorption enhancement factors as a function of translational velocity. EF = 4 implies that the hot CCl_4 molecules have a four times higher probability of scattering relative to the cold molecules.

The velocity selector used in this study transmits a 17% FWHM velocity distribution. The actual transmitted flux distributions for five velocity selector frequencies and two oven temperatues have been measured using TOF techniques and are shown in Fig. 6. At 125 Hz and 165 Hz the transmitted distributins essentially overlap for T_B = 298 K and 560 K. For higher frequencies the hot beam distributions are seen to shift to slightly higher velocities due to the slope of the T_B = 298 K Maxwell-Boltzmann distribution in that velocity range. The EF factors in Fig. 5 have been corrected for these shifts.

IV. DISCUSSION

The velocity dependence of EF as shown in Fig. 5 clearly indicates that the internal energy of a molecule becomes increasingly more important in determing its sticking probability as its translational energy is decreased. We have also demonstrated that this enhancement must be explained using a

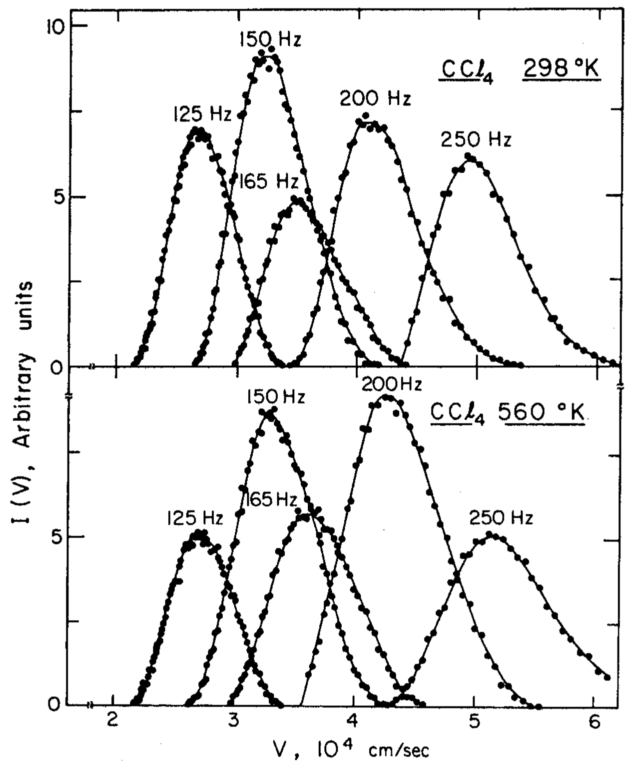

Fig. 6. Experimentally measured flux distributions transmitted by the velocity selector at the five settings used in the determination of EF.

dynamic collisional energy transfer model rather than a two-step adsorption/evaporation model which would imply cosine distributions for the scattered molecules as well as a non-linear dependence of scattered intensity on incident intensity. We do not observe either of the above (see, for example, Fig. 3) and will treat this question in more detail elsewhere.

V. CONCLUSION

It has been shown that the internal energy of a molecule can significantly influence its sticking probability upon collision with a cold surface. We are currently conducting experiments to explicitly obtain the velocity distribution of scattered molecules employing cross-correlation TOF techniques. A closed-cycle helium refrigerator has also been incorporated into our system to allow experiments with surface temperatures as low as 10 K to be carried out. We conclude this paper by mentioning that recently completed experiments with velocity selected SF_6 beam have revealed internal energy enhancement effects quite similar to those reported for CCl_4 in this paper.

VI. ACKNOWLEDGEMENT

This work was jointly supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy and Los Alamos Scientific Laboratory.

REFERENCES

1. S. T. Ceyer and G. A. Somorjai, Ann. Rev. Phys. Chem. 28, 477 (1977).
2. J. D. Doll, J. Chem. Phys. 66, 5709 (1977).
3. N. F. Basov, E. M. Belenov, V. A. Isakov, Yu. S. Leonov, E. P. Markin, A. N. Oraevskii, V. I. Romanenko, and N. B. Ferapontov, JETP Lett. 22, 102 (1975).
4. K. S. Kochelashvili, N. V. Karlov, A. N. Orlov, R. P. Petrov, Yu. N. Petrov, and A. M. Prokhorov, JETP Lett. 21, 302 (1975).
5. G. K. Anderson and J. T. Lee, submitted to Optics Letters.
6. Y. T. Lee, J. D. McDonald, P. R. Lebreton and D. R. Herschbach, Rev. Sci. Instrum. 40, 1402 (1969).
7. J. S. Ahearn, J. P. Monaghan, and J. W. Mitchell, Rev. Sci. Instrum. 41, 1853 (1970).
8. V. L. Hirschy and J. P. Aldridge, Rev. Sci. Instrum. 42, 381 (1971).
9. R. M. Logan and R. E. Stickney, J. Chem. Phys. 44, 195 (1966).