# Velocity Distribution of $H_2$, HD, and $D_2$ Molecules Desorbing from Polycrystalline Nickel Surfaces

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Velocity distributions of desorbing molecules have been measured as a function of both desorption angle, $\theta$, and surface temperature, $T_s$. The mean energy, $\bar{E}$, of $D_2$ desorbing from a half-sulfur-covered nickel surface at $T_s = 1143$ K decreases from $3.35kT_s$ at $\theta = 0°$ to $2kT_s$ at glancing desorption, whereas the speed ratio increases from values $< 1$ to values $\geq 1$. Over the range $940\ \text{K} < T_s < 1040$ K, $\bar{E}$ was proportional to $T_s$. No differences in mean energy and speed ratio for $H_2$, HD, or $D_2$ were observed.

Desorption of adsorbates from surfaces is one of the elementary processes of a gas-surface interaction. Experimental data on angular and velocity distributions of desorbing species, which are necessary to understand the physics of the desorption mechanism, are very scarce. The overwhelming part of the experimental information consists only of desorption-rate data. Van Willigen,[1] Palmer *et al.*,[2] and later Stickney and co-workers[3-5] have measured the angular distribution of the intensity of $H_2$, HD, and $D_2$ desorbing from a variety of metals. The main result of these experiments was that the angular distributions of intensity (measured from the surface normal, $\theta = 0$) are more or less strongly peaked in the direction of the normal, varying with $\cos^n\theta$ ($1 \leq n < 9$) rather than with $\cos\theta$ as expected for simple random emission. That such an emission could not vary with $\cos\theta$ had been predicted previously by starting from detailed-balance considerations.[6] In addition, Dabiri, Lee, and Stickney[5] observed that the mean kinetic energy of $D_2$ desorbing from a polycrystalline Ni surface in the direction of the normal was about 45% above the value expected from an equilibrium distribution at $T_s$. However, the time-of-flight (TOF) measurement of the velocity distribution function also showed that the speed ratio $S = (32/9\pi - 1)^{-1/2} \times (\langle V^2\rangle/\langle V\rangle^2 - 1)^{1/2}$ was $0.95 \pm 0.07$, which is not in contradiction with the value corresponding to a Maxwellian distribution ($S = 1$).

Van Willigen[1] proposed an "activated-adsorption model" (AA model) which, based upon detailed-balance arguments, explained the strongly peaked angular distributions of the experimentally observed intensity. This model is also in qualitative agreement with the high mean kinetic energy observed for $D_2$ molecules but is not in agreement with the measured speed ratio as it predicts $S \cong 0.45$ for the data of Dabiri, Lee, and Stickney.[5a] Another model, proposed by Goodman,[7] effectively assumes that the desorbed molecules have a Maxwellian-type distribution but with different temperatures $T_n$ and $T_t$ in the normal and tangential directions to the surface. Goodman does not believe his model to be "correct," but it was the simplest model which seemed to be consistent with the existing experimental data.[7] The model predicts $S = 1$ for any $T_n$, $T_t$ combination, in accord with Dabiri's observation. Recently Willis and Fitton[8] explained the strongly peaked angular distribution of the desorbed $H_2$ as an effect of the short-range dynamical screening of the substrate electrons which leads to a weakly bound hydrogen "quasi-molecule." However, their theory predicts a kinetic energy of 3-4 eV for the normally desorbed $H_2$ molecules, and this lies well beyond the range of observed energies. It is, however, difficult to make a definite choice between the existing models or to construct new models with the aid of the available data since the angular distribution of the intensity is relatively insensitive to the features of the proposed models. Moreover, the only existing TOF measurement,[5a] being restricted to merely one direction, can be interpreted in a number of ways.

Although it was recognized[7,9] that experimental data describing the kinetic energy of molecules as a function of the desorption angle would be valuable, no such work has yet been done. This is because the general difficulty of obtaining reasonable statistics in TOF measurements is made more severe in this particular case of strongly peaked angular distributions: As one moves away from the normal direction the intensity decreases as $\cos^{n-1}\theta$. We succeeded in these measurements by using a TOF apparatus with a signal-to-noise ratio about two orders of magnitude higher than that reported in Ref. 5a. In addition to the angular dependence of energy and speed ratio of the desorbed molecules, we also measured the dependence of energy and speed ratio on surface temperature ($T_s$).

The sample arrangement was similar to earlier experiments[1,3-5] where the hydrogen was supplied to the surface by diffusion through the polycrystalline nickel sample. The sample was surrounded by a resistance-heated oven which could be rotated to allow measurements of desorption as a function of $\theta$ ($0° \leqslant \theta \leqslant 70°$). The TOF apparatus consists of three differentially pumped chambers (main chamber with sample, chopper chamber, and detector chamber) evacuated by means of ion and titanium sublimation pumps. A detailed description will be presented elsewhere.[11] By use of a bakable magnetically suspended chopper[11] the background pressure could be greatly reduced in all three chambers (less than $5\times10^{-11}$ Torr). The desorption flux of $H_2$, HD, or $D_2$ from the sample raised the corresponding partial pressure in the main chamber to about $2\times10^{-8}$ Torr. However, the chopper and the detector chamber could both be kept in the $10^{-10}$-Torr range. This resulted in a high signal-to-noise ratio for the TOF measurements ($S/N = 1$ for $D_2$ and $S/N = \frac{1}{8}$ for $H_2$). In contrast to previous experiments,[5a] no measurable modulated background signal was detected when the pressure behind the heated sample was reduced while the pressure in the main chamber was maintained at $2\times10^{-8}$ Torr by introducing $H_2$ or $D_2$ through a leak valve.

A test of the TOF apparatus was performed with $D_2$ and $H_2$ originating from a Knudsen cell with a temperature of $972 \pm 2$ K. From an analysis of seven $D_2$ measurements we calculated $T_E = \bar{E}/2k = 976 \pm 2$ K and $\bar{S} = 0.977 \pm 0.004$.

The surface was cleaned by extended annealing of the sample at 1170 K. The surface composition was checked with Auger spectroscopy before and after each TOF measurement at the respective temperature. Nickel at elevated temperatures shows a surface segregation of sulfur with 50% surface coverage.[10] Within the temperature interval investigated this equilibrium coverage was found to be almost independent of the bulk concentration of sulfur and of temperature.[10] The previous TOF measurement[5a] was probably carried out with the same sulfur coverage. For other elements our Auger analysis showed the following maximal surface concentrations: Ca < 1%, Cd < 0.1%, and Sb < 1.3%. No other surface contaminants (e.g., carbon) could be detected. All results reported in this paper have been obtained with one and the same surface composition. The absence of cracks in the sample was tested by replacing the $H_2$ behind the heated sample with He at the same pressure. No change in the surrounding He pressure could be observed at the base pressure of $5\times10^{-11}$ Torr.

The mean energy $\bar{E}$ and speed ratio $S$ of $H_2$, HD, and $D_2$ desorbing at $\theta = 0°$ are shown in Fig. 1. The mean energy of these molecules clearly exceeds the thermal equilibrium value of $2kT_s$ being $3.35kT_s$. A comparison between experimental TOF curves and simulated curves (obtained from a Maxwellian distribution of same mean energy convoluted with the gate function) shows that they are very similar excepting the fact that the experimental curves are narrower ($S$ significantly lower than 1). The mean energy and speed ratio are the same for $H_2$, HD, and $D_2$ within the limit of error. (In making this comparison we used the error of the mean which confers to the conclusion a high degree of confidence. The bars in the figure represent this error and not the usual standard deviation.) The observed identity allowed us to use mainly $D_2$ in further experiments, which through improved S/N ratio made data collection with reasonable statistics easier.

The mean energy and speed ratio are shown as

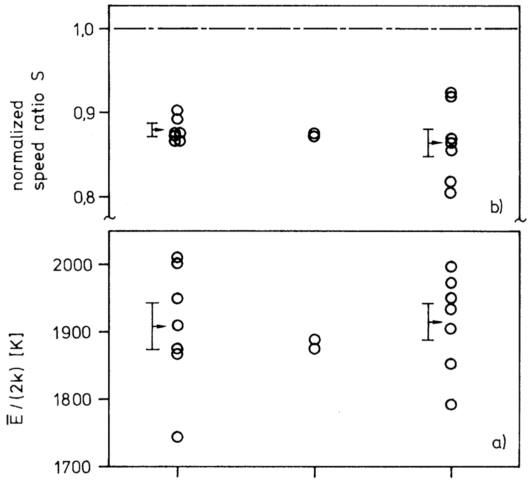

FIG. 1. (a) Mean energy $\bar{E}$ and (b) speed ratio $S$ for $H_2$, HD, and $D_2$ molecules desorbing normal to the surface at $T_s = 1143$ K. $\bar{E}$ is expressed in Kelvin by $T_E = \bar{E}/2k$. The mean values are $(T_E)_{H_2} = 1910 \pm 34$ K, $(T_E)_{D_2} = 1916 \pm 27$ K, $(T_E)_{HD} = 1884$ K; and $\bar{S}_{H_2} = 0.88 \pm 0.01$, $\bar{S}_{D_2} = 0.87 \pm 0.02$, $S_{HD} = 0.88$. The bars represent the *errors of the mean* (see text). In (b) the horizontal dash-dotted line corresponds to a Maxwellian distribution ($S = 1$).

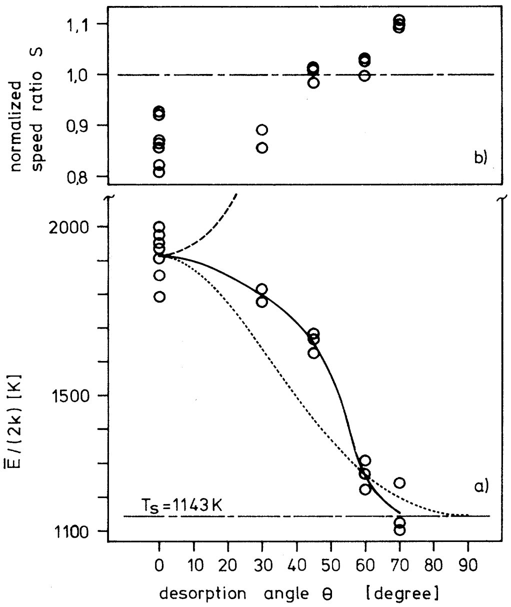

FIG. 2. (a) Mean energy $\bar{E}$ and (b) speed ratio $S$ vs desorption angle $\theta$ for $D_2$ molecules at $T_s = 1143$ K.

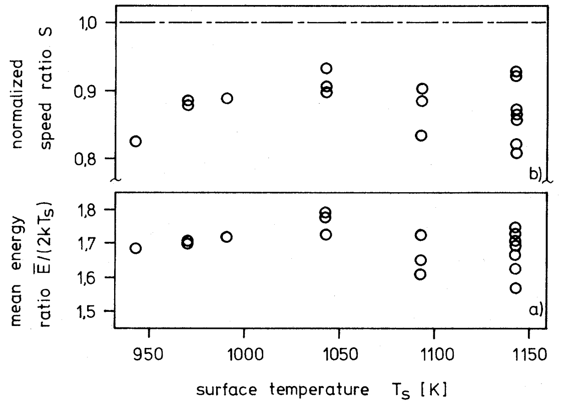

FIG. 3. (a) Energy ratio $\bar{E}/2kT_s$ and (b) speed ratio $S$ vs surface temperature $T_s$ for $D_2$. The mean values are $\langle \bar{E}/2kT_s \rangle = 1.70 \pm 0.01_5$ and $S = 0.88 \pm 0.01$ for 943 K $\leq T_s \leq 1143$ K.

a function of angle $\theta$ in Fig. 2, again for a surface temperature of 1143 K. With increasing desorption angle the mean energy decreases and approaches the value corresponding to the surface temperature. The speed ratio, however, increases with increasing angle. As the statistics become poorer with increasing desorption angle, it is for the moment not possible to make a definite statement whether the speed ratio only approaches the value unity or even increases beyond it. A further source of uncertainty is possible deviation of the surface from a geometrical plane which for polycrystalline surfaces is not unlikely: At great desorption angles any unevenness may lead to an apparent increase of mean energy and speed ratio. It would be thus worthwhile to obtain more exact data at great angles especially on monocrystalline surfaces. Indeed by looking at the results in Fig. 2 one gets the feeling that the molecules desorbing at glancing angles have, in contrast to those desorbing in the normal direction, characteristics corresponding to a Maxwellian distribution at $T_s$. A confirmation or negation of this impression would be important for the understanding of the desorption phenomenon. Measurements on monocrystalline surfaces might show a possible influence of surface structure.

The energy ratio $(\bar{E}/2kT_s)$ and the speed ratio for the molecules desorbing normal to the surface as a function of surface temperature are shown in Fig. 3. In the temperature range accessible to the measurement and within the limit of the errors both ratios seem to be independent of surface temperature. The mean values for 943 K $\leq T_s \leq$ 1143 K are $\langle \bar{E}/2kT_s \rangle = 1.70 \pm 0.01_5$ and $\bar{S} = 0.88 \pm 0.01$.

The intensity as a function of the angle $\theta$ was calculated from the flux measured in the TOF experiments. A direct measurement of the chopped beam with a lock-in amplifier was also carried out. By correcting the lock-in values for the detection probability dependence on molecule velocity, both methods gave approximately the same dependence: $\cos^{3.5}\theta$. This agreement is considered as a supplementary confirmation for the correctness of the measurements.

It is noteworthy that in most previously published measurements the intensity figures were deduced from the measured number density values by assuming an angle-independent energy distribution of the desorbing molecules. As $\bar{E}$ is strongly angle dependent the angular intensity distributions obtained in this manner have to be considered with caution.

The dependence of mean energy and speed ratio of the desorbing molecules on angle and on surface temperature reported here are in flagrant contradiction to the predictions of the AA model.[1,4] Indeed, the dashed line in Fig. 2(a) which corresponds to the prediction of the AA model has an opposite trend to the experimental data. The speed ratio predicted by this model falls far outside the Fig. 2(b) as it decreases from $S = 0.475$ for $\theta = 0°$ to $S = 0$ for $\theta = 90°$. Finally the independence of the energy ratio (Fig. 3) on surface temperature is also in contradiction with the AA model (the model predicts a decrease of the energy ratio with increasing temperature). On the other hand, the model proposed by Goodman[7] is in qualitative agreement with most experimental data reported here: The dotted line in Fig. 2(a) predicted by Goodman's model for $T_n = 1916$ K and $T_t = 1143$ K reflects correctly the experimental trend. The constancy of the energy ratio is, within the limits of the error, not in contradiction with this theory. The only discrepancy appears when looking at the speed ratio values: Goodman's model predicts in all cases $S = 1$ which is in contradiction with all our data for small $\theta$ in Figs. 1(b), 2(b), and 3(b).

The fact that the results for $H_2$, HD, and $D_2$ are practically identical is probably valid not only in the particular case of this experiment. It seems that the detailed features of the desorption process (energy distribution, angular dependences, etc.) are due neither to excitations of rotational or vibrational states nor to other molecular mass-dependent phenomena but to the chemisorption mechanism itself. This general observation and the peculiarities of the data presented here might be useful for the construction of more realistic models for the associative desorption process. Further experiments with monocrystalline surfaces and variable sulfur coverage are in progress.

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[1] W. Van Willigen, Phys. Lett. 28A, 80 (1968).

[2] R. L. Palmer, Joe N. Smith, Jr., H. Saltsburg, and D. R. O'Keefe, J. Chem. Phys. 53, 1666 (1970).

[3] T. L. Bradley, A. E. Dabiri, and R. E. Stickney, Surf. Sci. 29, 590 (1972).

[4] T. L. Bradley and R. E. Stickney, Surf. Sci. 38, 313 (1973).

[5a] A. E. Dabiri, T. J. Lee, and R. E. Stickney, Surf. Sci. 26, 522 (1971).

[5b] T. E. Kenny, A. E. Dabiri, and R. E. Stickney, Researh Laboratory of Electronics, MIT, Quarterly Progress Report No. 102, July 1971 (unpublished).

[6] George Comsa, J. Chem. Phys. 48, 3235 (1968).

[7] F. O. Goodman, Surf. Sci. 30, 525 (1972).

[8] R. F. Willis and B. Fitton, Astrophys. Space Sci. 34, 57 (1975).

[9] M. J. Cardillo, M. Balooch, and R. E. Stickney, Surf. Sci. 50, 263 (1975).

[10] M. Perdereau, Surf. Sci. 24, 239 (1971).

[11] K. Boden, George Comsa, R. David, J. K. Fremerey, and K. D. Rendulic, to be published.

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# Solitons in a Coupled Linear Chain System*

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The existence of solitons in two or more dimensions is discussed. Solitary-wave solutions are found for a system of discrete chains with a derivative of a periodic coupling between the chains. Relevance of the model to phase solitons in the Peierls condensate and in spin systems is discussed.

Recent studies have indicated the possible importance of solitons and solitary waves[1] in the dynamics of structural phase transitions[2-4] and in the low-temperature conductiviy of one-dimensional conductors.[5,6] However, applicability of these ideas to real systems is limited because static soliton solutions were found only in strictly one-dimensional systems. Moreover, for higher dimensional continuous media with an elastic coupling $(\nabla\varphi)^2$ it is known that there are no static, finite-energy solitons.[7,8] In