

# Recombinative desorption of H<sub>2</sub> and D<sub>2</sub> from Cu(110) and Cu(111): Determination of nonequilibrium rovibrational distributions<sup>a)</sup>

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When the adsorption probability of molecules colliding with a surface is unity and independent of the distribution of molecular internal states, orientations, and velocities, equilibrium statistical mechanics predicts that the molecular quantum state distributions in desorption will be governed solely by the surface temperature  $T_s$ . Often, however, this is not the case because the chemisorption process *does* depend on the details of the motion during the molecule-surface encounter. Then it follows by detailed balance that the dynamical behavior is reflected in the distribution of molecular quantum states in desorption. The determination of these distributions, therefore, can elucidate the nature of those special forces and configurations experienced by the desorption flux. An example of such "nonthermal" desorption is that of the activated recombinative desorption of molecular hydrogen from copper surfaces, where much has been learned by studying the properties associated with molecular center-of-mass motion.<sup>1-3</sup> Clearly, a more complete understanding of the recombinative desorption dynamics of H<sub>2</sub> from Cu will be gained by studying rotational and vibrational state distributions as well.

In this letter we report the rovibrational quantum state distributions of H<sub>2</sub> and D<sub>2</sub> recombinatively desorbing from clean, single-crystal Cu(110) and Cu(111). Experiments are performed in an ultra-high vacuum apparatus, described previously.<sup>4</sup> Modifications of this apparatus will be presented in detail elsewhere.<sup>5</sup> Briefly, H<sub>2</sub> or D<sub>2</sub> molecules are supplied to the sample surface via atomic permeation through ~0.5 mm Cu thicknesses at temperatures between 830–1000 K. The sample disks are prepared by electro-discharge milling from 99.999% pure single-crystal cylinders. The surfaces are oriented to within 1° of the (110) or (111) faces, chemically polished,<sup>6</sup> and sputter cleaned. Sample cleanliness and crystalline order are verified at approximately 3 h intervals during a permeation experiment by Auger electron spectroscopy and low energy electron diffraction.

Rovibrational state distributions of the recombinatively desorbing H<sub>2</sub> and D<sub>2</sub> are determined via a 2 + 1 resonance-enhanced multiphoton ionization technique.<sup>7</sup> State-selective ionization is accomplished by two-photon excitation  $E, F^1\Sigma_g^+ \leftarrow X^1\Sigma_g^+$  using  $\lambda_1 \cong 193$  nm and  $\lambda_2 \cong 211$  nm, followed by efficient one-photon ionization  $H_2^+ X^2\Sigma_g^+ + e^- \leftarrow H_2 X^1\Sigma_g^+$  and time-of-flight detection. Wavelengths at  $\lambda_1$  (~2 cm<sup>-1</sup> FWHM, ~100  $\mu$ J) and  $\lambda_2$  (~2 cm<sup>-1</sup> FWHM, ~300  $\mu$ J) are generated via stimulated Raman scattering (in H<sub>2</sub>) of a frequency-doubled dye laser. Figure 1 shows typical spectra of both H<sub>2</sub> and D<sub>2</sub> desorbed from Cu(111). The accuracy of this method for determining rotational populations has been verified by analyzing spectra obtained from a heated nozzle source (300–

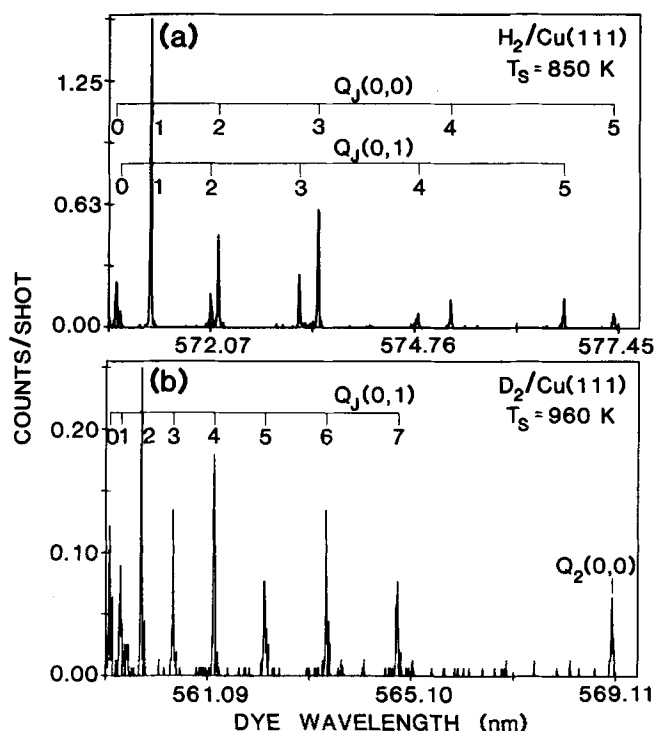


FIG. 1. Resonance-enhanced multiphoton ionization spectra of (a) H<sub>2</sub> desorbing from Cu(111) at  $T_s = 850$  K and (b) D<sub>2</sub> desorbing from Cu(111) at  $T_s = 960$  K.

2000 K), and the results are in accord with previous experiments.<sup>8</sup> The nozzle is also used as a vibrational population standard to calibrate the measured  $Q_J(0,1)/Q_J(0,0)$  signal ratios against vibrational temperature.

Figure 2 presents the H<sub>2</sub> and D<sub>2</sub> rotational distributions determined following recombinative desorption from Cu(111) and Cu(110). Each set of points represents the sum of approximately 10–20 averaged 45 min data sets. The figure is a plot of the quantity  $\ln\{IQ_J/[g_n(2J+1)]\}$  vs  $E_J$  where  $IQ_J$  is the power-normalized intensity of  $Q$  branch member  $J$ ,  $g_n$  is its nuclear spin degeneracy,  $(2J+1)$  is the corresponding rotational degeneracy and  $E_J$  is its rotational energy. A Boltzmann distribution would appear as a straight line and the line corresponding to a rotational temperature  $T_R$  equal to  $T_s = 850$  K is plotted for reference. The following points emerge from this figure: (i) the H<sub>2</sub> and D<sub>2</sub> rotational distributions are not accurately represented by a temperature although the deviation from Boltzmann behavior is not dramatic; (ii) the mean rotational energy is less than  $T_s$ ; (iii) the H<sub>2</sub> and D<sub>2</sub> distributions are identical to within the accuracy of the data; (iv) the Cu(110) data are identical to the Cu(111) data to within the experimental accuracy; (v) the H<sub>2</sub> data for  $v'' = 0$  and  $v'' = 1$  show no systematic differences;

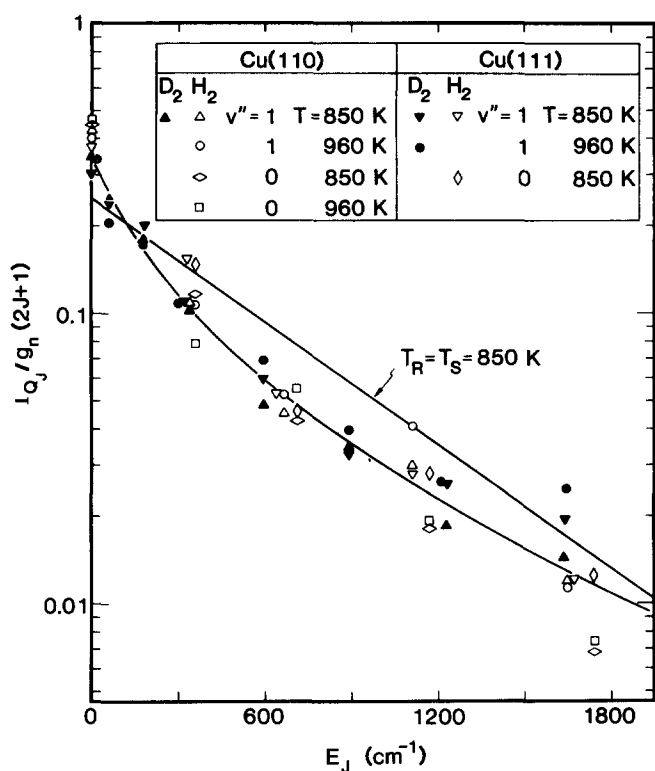


FIG. 2. Summary of all rotational population data in the form of a Boltzmann plot of normalized rotational line intensity vs rotational energy  $E_J$  of the state  $J$ . The  $T_R = T_s$  line is plotted for reference and the curve through the data points is drawn simply to aid the eye. See key for definition of symbols.

(vi) *ortho* and *para* forms of both  $H_2$  and  $D_2$  lie along common curves, meaning they are populated statistically; and (vii) no systematic differences are noted for the two surface temperatures studied.

Inspection of Fig. 1 suggests that a substantial fraction of the desorption flux is vibrationally excited. Comparison of the experimentally measured  $Q_J(0,1)/Q_J(0,0)$  desorption ratios with those measured in the calibration nozzle source shows the  $(v''=1)/(v''=0)$  population ratios to be  $0.052 \pm 0.014$  and  $0.24 \pm 0.20$  for  $H_2$  and  $D_2$ , respectively, from the (110) face, and  $0.084 \pm 0.030$  and  $0.35 \pm 0.20$  for  $H_2$  and  $D_2$  from the (111) face. The velocity distributions for

both vibrational levels are taken to be equal; we estimate<sup>9</sup> that this assumption could decrease these ratios by no more than a factor of 2. In contrast, the vibrational population ratios in equilibrium at  $T_s = 850$  K are 0.0009 for  $H_2$  and 0.0063 for  $D_2$ . Hence activated recombinative desorption of  $H_2$  and  $D_2$  from these surfaces results in vibrational excitation some 50–100 times greater than that expected if all molecular degrees of freedom were in equilibrium at  $T_s$ ! If detailed balance is valid for this system,<sup>10</sup> greatly enhanced sticking coefficients for  $v'' = 1$  would be predicted. The simple notion that placing energy along the bond-rupturing coordinate of a molecule enhances its dissociation probability seems to be borne out. Molecular rotation, in comparison, has a much less pronounced effect as evidenced by the mild, though significant, departure from  $T_R = T_s$ . The present study is the first example of marked nonequilibrium rotational and vibrational behavior in recombinative desorption from clean metal surfaces, although similar behavior has been reported for  $N_2$  desorption from sulfur-covered polycrystalline Fe.<sup>11</sup>

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