celeration of the electrons must take place before the ion-acoustic instability saturates. This latter condition gives $T_c \equiv L_c/v_d < T_s$ where T_s is the time for the ion-acoustic instability to saturate. In fact, this requirement is satisfied for the simulations using $L = 1024\lambda_D$ and $512\lambda_D$.

To check this point we have performed another simulation with $v_d = 0.3v_{te}$ and $L = 1024\lambda_D$. The result has shown the presence of acoustic anomalous resistivity ($\eta_a/\eta_0 = 3.8 \times 10^{-5}$) until $t\omega_{pe} \approx 750$ but after the saturation of the instability, it reduced to the classical value ($\eta_c/\eta_0 = 1.3 \times 10^{-5}$) and no double layers were formed. Using $v_d = 0.3v_{te}$ and $L = 1024\lambda_D$ we find $T_c \approx 3300\omega_{pe}^{-1}$. At this time, the acoustic instability has saturated and no more anomalous resistivity is present and therefore $T_c < T_s$ is not satisfied.

While periodic boundary conditions are used for the simulations reported here, we believe they are not important for a sufficiently long system, since the electrons had no chance to return before the double layer was formed. In support of this, two more simulations were carried out with and without the use of the periodic boundary conditions with the system length of 4096 Debye lengths. The results indicate that formation of double layers for both cases are similar to each other. It appears, however, that the use of periodic boundary condition will shorten the lifetime of double layers by mixing the upstream electrons with the downstream electrons.

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Internal Energy of Heterogeneous Reaction Products: Nitrogen-Atom Recombination on Iron

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Electron-beam–induced fluorescence has been used to measure the vibrational energy of nitrogen molecules desorbing from a polycrystalline iron surface, following atomic permeation and recombination on the iron surface. The vibrational temperature of the desorbing nitrogen is found to be significantly greater than the temperature of the iron surface, indicating that a fraction of the nitrogen-atom recombination energy remains with the desorbing nitrogen molecule as internal excitation.

Characterization of the reaction dynamics in heterogeneous systems requires a knowledge of the energy state of the heterogeneous reaction products. Ideally, one would like to know the translational- and internal-energy–state distribution, as well as the spatial distribution of desorb-

ing product species. This energy and angular information can be very useful in describing the detailed dynamics of reactions taking place on solid surfaces. Some effort has been made to obtain angular distributions of heterogeneous reaction products.[1] In addition, the translational

energy of desorbing product molecules has been determined in a few cases.[2] We report here the first direct measurement of product internal energy in a heterogeneous reaction. Specifically, we have measured the vibrational energy of nitrogen molecules produced by the recombination of nitrogen atoms on an iron surface. We find the nitrogen molecules to be significantly excited vibrationally.

Experimental measurements of hydrogen permeation and recombination angular distributions[1] and translational energies,[3] in combination with theoretical studies of hydrogen-atom surface recombination dynamics, suggest the possibility of internal excitation of molecules desorbing from a surface following an exothermic reaction. In particular, when there is an activation energy for dissociative adsorption, as is the case for hydrogen on copper[4] and nitrogen on iron,[5] the relaxation of reaction energy into the solid appears to be less likely. In order to obtain a more detailed understanding of the dynamics of exothermic heterogeneous reactions such as these, the experiments reported here were undertaken.

The experimental apparatus used for these measurements is illustrated schematically in Fig. 1. The source is a high-purity (Materials Research Corporation 99.99% purity) polycrystalline iron rod machined to give a membrane 0.010 in. thick on the end of a 0.5-in.-diameter tube. This tube is welded to a stainless-steel fitting in the center of the 6-in. source flange. The tube and membrane are heated by radiation from a tungsten coil heater surrounding the source tube.
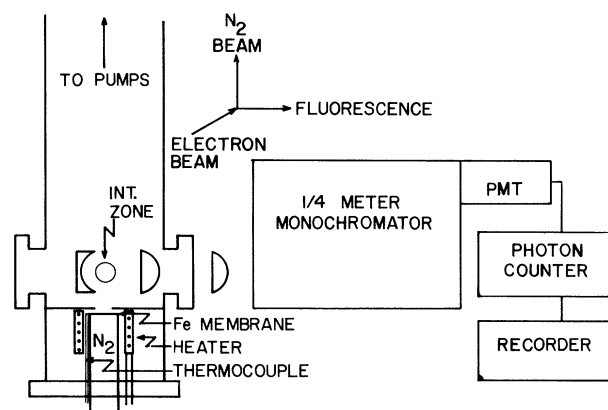

FIG. 1. Schematic diagram of experimental system used in these studies. N_2 desorbing from the iron membrane is excited by an electron beam in the interaction zone. The fluorescence emission is focused on the entrance slit of the monochromator.

The temperature of the iron surface is measured by means of a W-5%Re/W-26%Re thermocouple spot welded to the edge of the tube, or alternatively with an optical pyrometer. Nitrogen is introduced to the backside of the heated iron membrane at a pressure of about 1.3 atm. Nitrogen molecules adsorb dissociatively on the hot surface and permeate the iron atomically at a rate determined by the iron temperature, the activation energy for diffusion of nitrogen atoms in iron,[6] the membrane thickness, and the pressure differential across the source. Nitrogen atoms permeating this iron membrane recombine on the vacuum side of the source and desorb. The desorbing molecules enter the interaction zone indicated in Fig. 1.

In this region, the nitrogen molecules formed by recombination of nitrogen atoms on the iron surface interact with an electron beam. The beam has an energy of 2100 eV and a current of 8 mA in the interaction zone. Nitrogen molecules in the electronic ground state, $N_2 X^1\Sigma_g^+$, are ionized by collisions with these electrons and left in the electronically excited $N_2^+ B^2\Sigma_u^+$ state. This state fluoresces to the $N_2^+ X^2\Sigma_g^+$, and the fluorescence emission is collected and focused on the entrance slit of a $\frac{1}{4}$-m Jarrel-Ash grating monochromator. The dispersed light is detected with a Hamamatsu R585 photomultiplier. The output of the photomultiplier is then counted as individual photon events, by a Hewlett Packard Model 5300 Universal Counter/Timer following amplification and shaping with a Pacific Precision AD-6 amplifier-discriminator. The analog output of this counter is recorded on a strip-chart recorder.

The ratio of vibrational-band intensities in the N_2^+ fluorescence spectrum can then be used to assign a vibrational temperature to the nitrogen molecules desorbing from the iron surface. This technique, electron-beam–induced fluorescence,[7] has been used for a number of years as an internal state diagnostic for rarefied gas flows. The excitation and emission process is well understood, and has been used for reliable measurements of vibrational,[7] rotational,[8] and in favorable cases translational[9] energies for some time. In addition, we have checked the technique by measurement of the vibrational and rotational temperatures of backfilled nitrogen (10^{-6} Torr) in our system. We obtain the room-temperature internal temperature when the system is backfilled at room temperature. The measured internal temperature from backfill spectra also agree with

the system temperature when it is increased by operating the source heater with no nitrogen behind the iron surface.

Figure 2 shows the region of the N_2^+ $B^2\Sigma_u^+$ to N_2^+ $X^2\Sigma_g^+$ transition between 340 and 460 nm for nitrogen desorbing after permeation and recombination on the iron surface at 1150 °K. The 0-0, 0-1, and 1-0 vibrational bands of N_2^+ are clearly visible, as well as two CO^+ (comet-tail system) vibrational bands from background CO. The equivalent pressure of N_2 in the interaction zone at this membrane temperature is 8×10^{-8} Torr. This spectrum has been corrected for background emission from the hot surface. In addition, prior to the vibrational-temperature determination, overlapping contributions from the 5-0 and 2-0 CO^+ transitions were subtracted from the N_2^+ 1-0 and 0-1 peaks. The vibrational temperature obtained by comparison of the measured ratio of the 0-0 and 1-0 transition intensities to the ratio predicted for a Boltzmann population is 2600 °K. Based on the 0-1 to 1-0 ratio the vibrational temperature is 2600 °K for this spectrum. The agreement between these numbers indicates that there is no interference between the CO^+-background-gas fluorescence and that of the N_2^+.

This measurement was repeated several times in the surface-temperature range of 1150 to 1325 °K with four separate iron source membranes. The results of these measurements are presented in Table I. In each case, the vibrational temperature determined shortly after mounting a new source and bringing it to the surface temperature of interest was significantly greater than that

surface temperature. As the measurement was repeated for a particular iron membrane, the vibrational temperature tended to decrease irreversibly. This occurred when successive spectra were taken with the surface temperature increasing, with it remaining constant, or when the surface temperature was decreasing. The measured vibrational temperature appeared to decrease with the time during which the source was hot, approaching a vibrational temperature (1250 °K) in the region of the surface temperature after prolonged heating.

This irreversible change in measured vibrational temperature, from a temperature ~1000 °K greater than the surface temperature immediately after initial heating, to a vibrational temperature nearer that of the surface after extended heating, suggested an irreversible change in the surface composition or structure of the iron membrane. In order to test this possibility, a freshly prepared source membrane was mounted in a separate UHV system having an Auger spectrometer. This membrane was subjected to the same heating history as the four membranes used for the vibrational-temperature measurements, and the surface composition was followed with the Auger spectrometer. Immediately after heating the iron above 1000 °K, the Auger spec-
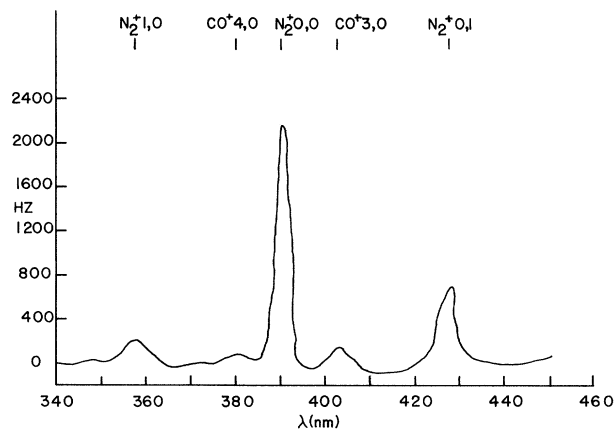

FIG. 2. Fluorescence spectrum from 350 to 430 nm after background subtraction. Intensities used for temperature determination are corrected for overlapping CO contributions.

TABLE I. Nitrogen vibrational temperature following atom recombination on four iron surfaces. For each membrane, the time after initial heating is given with the corresponding vibrational temperature, T_v (°K) (± 200 °K), and surface temperature, T_s (°K) (± 20 °K).

Membrane	Time (h)	T_v / T_s
No. 1	1	2600/1150
	90	1250/1170
	230	1200/1240
No. 2	16	2600/1170
	21	2400/1230
	35	1750/1230
	42	1800/1245
	47	1200/1200
No. 3	1.5	2150/1220
	2.5	1575/1220
	2.8	1400/1220
	4.0	1250/1290
No. 4	22	1500/1215
	115	1450/1230
	117	1600/1280
	120	1550/1325
	122	1300/1325

trum showed sulfur as the major impurity, at a level equivalent to about 30% of a monolayer. The sulfur coverage decreased as the surface was heated. These measurements indicate a dependence of the N_2 vibrational temperature on the surface sulfur coverage.

The measured vibrational temperature of N_2 desorbing from the freshly mounted iron membrane is about 1000 °K greater than the iron surface temperature. This 1000 °K corresponds to an energy of about 2 kcal which is ~1% of the nitrogen-atom recombination energy. Studies of nitrogen adsorption and thermal desorption from clean single crystals of iron by Boszo et al.[5] indicate that the dissociative adsorption of nitrogen on (100) and (110) iron is activated by about 5 kcal/mole. On the (111) face, the adsorption appears to be nonactivated. Since the polycrystalline iron surface used in the present study appears to be sulfur contaminated, the increased vibrational temperature observed here may be an indication of an effective activation barrier on the polycrystalline surface, appearing as excess vibrational energy in the reaction-product molecules. The apparent dependence of the measured vibrational temperature on the heating time could be the result of a temperature-dependent change in surface composition as suggested by the Auger measurements discussed above.

The observation of a vibrational temperature for nitrogen greater than the temperature of the surface indicates a very short surface-residence time for the nitrogen molecules formed by atom recombination. This suggests that the atom recombination-desorption process is a concerted one on this surface. This conclusion is in agreement with the work of Rosner et al.,[10] who have obtained evidence for internally excited molecules desorbing from a surface after atom recombination by an indirect method.

Measurement of the rotational and translational energy of the desorbing molecules would be useful in obtaining a more complete description of nitrogen-atom recombination on iron. The electron-beam–induced fluorescence technique offers the possibility of determining the rotational state of the desorbing nitrogen molecules by resolution of the rotational structure of the 0-0 vibrational band. It may also be possible, by means of Doppler-shift measurements of the 0-0 band position, to assign a translational temperature to the desorbing nitrogen molecules. These measurements, presently underway in our lab-

oratory, should help considerably in obtaining a detailed understanding of the dynamics of this recombination reaction. In addition, in situ determination of the effect of surface composition and surface structure on the degree of internal excitation in this system, with use of soft–x-ray appearance-potential spectroscopy and single-crystal surfaces, is underway.

We have reported here the first direct measurement of the internal-energy state of a heterogeneous reaction product. Using the technique of electron-beam–induced fluorescence, we have determined the vibrational temperature of nitrogen molecules formed by the recombination of nitrogen atoms on iron which is apparently sulfur contaminated, and found it to be about 1000 °K greater than the temperature of the surface on which they are formed. This measured vibrational temperature appears to decrease as sulfur is removed from the iron surface. From these measurements we conclude that the nitrogen molecules have a very short residence time on this surface following a concerted recombination reaction.

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