

Alkali-Metal Promotion of a Dissociation Precursor: N₂ on Fe(111)

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(Received 23 December 1985)

The vibrational and thermal-desorption spectra of the terminal and π -bonded adsorption states of N₂ on clean and potassium-promoted Fe(111) at 74 K are reported. Submonolayer precoverages of potassium dramatically enhance the sticking coefficient of α_1 -N₂, the π -bonded precursor to dissociation. As potassium promotion of surface reactions has been previously attributed to bond weakening in the dissociation precursor, an increase of the precursor population, with no evident bond weakening, is an important new result.

PACS numbers: 82.65.Jv, 82.30.Lp, 82.80.Pv

A major goal of surface physics is to elucidate the detailed physical mechanisms involved in heterogeneous catalysis. The aim is to understand not only specific systems that are of catalytic relevance, but also effects such as alkali-metal promotion that are important to many catalytic systems. Recently it has been shown¹ that the kinetics of N₂ adsorption and dissociation on K-precovered Fe(111) in ultrahigh vacuum (UHV) can be used to predict the ammonia synthesis rate in a catalytic reactor under industrial conditions (150–300 atm, 375–500 °C) where the dissociation of N₂ is believed to be the rate-limiting step.² Results from the Fe(111) surface were used since this crystal face shows the highest activity for N₂ chemisorption³ and high-pressure synthesis,⁴ and many of the kinetic parameters of this system have been determined.^{5–7}

Recent work using low adsorption temperatures and UHV surface analytical techniques has identified a number of intermediates involved in the adsorption and dissociation of N₂ on clean and K-promoted Fe(111), including the precursors to dissociation.^{6–10} The α state, which desorbs from the clean surface at ≈ 150 K¹¹ and has an unusually low N–N stretch frequency (< 1500 cm⁻¹),⁸ has been attributed to N₂ π bonded to the surface.⁸ At higher temperatures this state is the immediate precursor to dissociation.^{6,8} Adsorption of the α state on a K-precovered surface at temperatures ≥ 100 K results in the appearance of an additional K-induced π -bonded species, denoted the α_2 state, characterized by a stronger Fe–N₂ bond and a weakened N–N bond.^{9,10} The more weakly held γ state, which desorbs from the clean surface at ≈ 90 K,^{6,7} has been shown by x-ray photoelectron spectroscopy (XPS) to be N₂ bonded with its axis normal to the surface.^{6,8} The γ state has been shown to be the adsorption precursor to the α state,^{6,7} but the precise nature of this species has yet to be determined. To our knowledge, the effects of K on this state have not

been reported.

In this Letter we present results that contribute to the understanding of N₂ adsorption on Fe(111), and observe a surprising new effect of K coadsorption which we believe may be of importance to other dissociative systems as well. We report the vibrational spectrum of the γ state for the first time, identifying this state as terminally bonded N₂. More importantly, we find that low precoverages of K dramatically increase the sticking coefficient of the π -bonded N₂ dissociation precursor (the α_1 state), without significantly weakening the N–N bond. The conclusions are based on our studies of ¹⁵N₂ adsorbed at 74 K on clean and K-precovered Fe(111), using low-energy electron diffraction (LEED), thermal-desorption spectroscopy (TDS), and high-resolution electron-energy-loss spectroscopy (HREELS).

The experiments were carried out in an ion, turbomolecular, and titanium sublimation pumped two-level stainless-steel UHV system with a base pressure of 4×10^{-11} Torr. A sample temperature of 74 K could be maintained for ≈ 45 min by pumping on a liquid-nitrogen reservoir in thermal contact with the sample mount. The sample was prepared and cleaned following previously described procedures.³ A clean surface was characterized by a sharp, low-background (1 \times 1) LEED pattern and a HREELS spectrum without contaminant vibrations. Potassium was evaporated from a SAES getter source onto a cold (85 K) Fe(111) surface, which was subsequently annealed to ≈ 700 K for 2 min to achieve a well-ordered K overlayer. The annealing temperatures were chosen to desorb K in excess of the desired coverages.¹² A K coverage of 0.11 monolayer (ML, where 1 ML $\equiv 7.1 \times 10^{14}$ cm⁻² corresponds to one adsorbate molecule per first-layer substrate atom) was characterized by a sharp (3 \times 3) LEED pattern,¹³ while other K coverages were determined from the N₂ TDS data as

described below. All TDS spectra were recorded with a heating rate of $5.5 \text{ K} \cdot \text{s}^{-1}$, and all HREELS spectra were recorded in the specular direction with an angle of incidence of 60° with respect to the surface normal and a primary beam energy of 4.8 eV uncorrected for work function. Typical resolution was 65 cm^{-1} at full width at half maximum with $(1-5) \times 10^4 \text{ counts} \cdot \text{s}^{-1}$ in the elastically scattered peak. All HREELS spectra shown have been normalized to the elastic-peak intensity. Except as noted, all spectra were recorded for 30 min immediately after exposure of the surface at 74 K to $10 \times 10^{-6} \text{ Torr} \cdot \text{s}$ of $^{15}\text{N}_2$.

Figure 1 displays a series of HREELS vibrational spectra showing the transition from molecular to atomic nitrogen. In curve *a*, with a N_2 coverage of $\approx 1 \text{ ML}$,⁶ we attribute the mode at 2100 cm^{-1} to the N-N stretch of $\gamma\text{-N}_2$ (shifted down from 2331 cm^{-1} for the gas-phase molecule). The sensitivity of stretching frequencies to bonding coordination number,¹⁴ combined with knowledge of the Fe(111) surface topology,¹⁵ results in the assignment of $\gamma\text{-N}_2$ as terminally bonded to a first-layer Fe atom.¹² The small peak at 1415 cm^{-1} is the N-N stretch of the π -bonded α state, a small amount of which coexists with the γ state at this temperature.^{6,7} The thermal-desorption spectrum for this surface is reproduced in Fig. 2, curve *a*, showing the γ peak at 94 K and a small α peak at 145 K . As shown in Fig. 1, curve *b*, heating the surface temporarily to 110 K desorbs most of the $\gamma\text{-N}_2$ and converts the rest to $\alpha\text{-N}_2$,⁶ resulting in the (2.2 ± 0.7) -

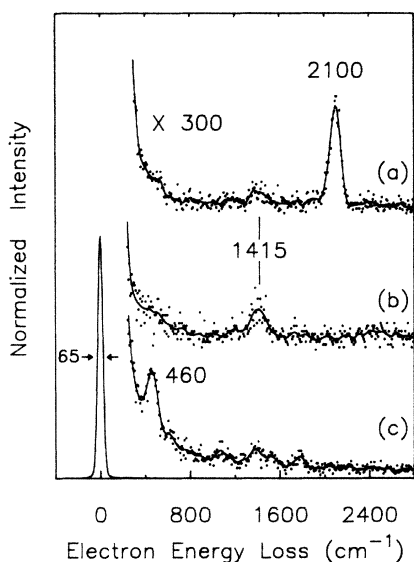


FIG. 1. HREELS data for (curve *a*) $^{15}\text{N}_2$ adsorbed on Fe(111) at 74 K , showing the $\gamma\text{-N}_2$ N-N stretch at 2100 cm^{-1} , (curve *b*) after heating to 110 K only the N-N stretch of $\alpha\text{-N}_2$ is observed, and (curve *c*) after heating to 160 K only the Fe-N stretch of atomic nitrogen is observed.

fold enhancement of the α N-N stretch remaining at 1415 cm^{-1} . The temperature-induced increase in the $\alpha\text{-N}_2$ coverage confirms that the system is not in equilibrium at 74 K .^{6,7} Furthermore, saturation of the surface with N_2 at 74 K does not lead to saturation of the α state within the elapsed time of the experiment. As measured by TDS, only $0.06 \pm 0.02 \text{ ML}$ of $\alpha\text{-N}_2$ was obtained, as compared with the known⁶ α saturation coverage of $0.10 \pm 0.03 \text{ ML}$. Following a temperature rise to 160 K , which leads to parallel desorption and dissociation of the remaining α ,⁸ Fig. 1, curve *c*, was recorded, showing the Fe-N vibration as expected at 460 cm^{-1} .^{8,10} The small loss feature apparent at $\approx 1100 \text{ cm}^{-1}$ has been positively identified as an Fe-H vibration,¹² while those at ≈ 1500 and $\approx 1800 \text{ cm}^{-1}$ are due to contaminant CO.¹⁵

In Figs. 2 and 3, sequences of TDS and HREELS spectra, respectively, are displayed, showing the effects of increasing precoverages of K. For the K-dosed surfaces (curves *b-d*), the TDS spectra were recorded immediately after HREELS. As the K precoverage is increased from 0 to $0.16 \pm 0.05 \text{ ML}$ in Fig. 2, we observe a (2.4 ± 1.0) -fold decrease in desorption of $\gamma\text{-N}_2$, from 0.96 ± 0.29 to $0.40 \pm 0.12 \text{ ML}$. Concurrently, we observe a (4.8 ± 2.1) -fold increase in α_1 (corresponding to the peak previously denoted α on the clean surface), from 0.06 ± 0.02 to $0.29 \pm 0.09 \text{ ML}$, along with the appearance of a new high-temperature

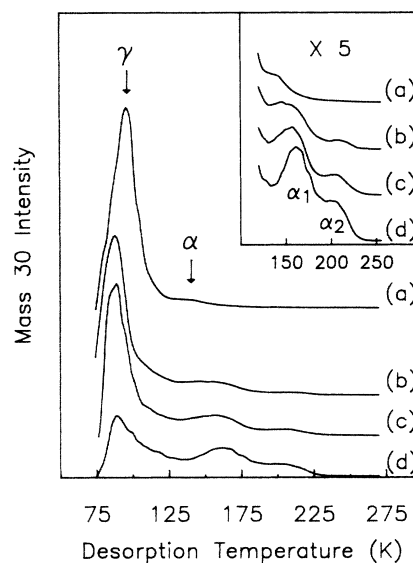


FIG. 2. TDS data for Fe(111) at 74 K exposed to $10 \times 10^{-6} \text{ Torr} \cdot \text{s}$ of $^{15}\text{N}_2$ with (curve *a*) an initially clean surface, and surfaces precovered with (curve *b*) 0.04 ± 0.02 , (curve *c*) 0.11 ± 0.02 , and (curve *d*) $0.16 \pm 0.05 \text{ ML}$ potassium, showing desorption from the low-temperature γ state and higher-temperature α_1 and α_2 states. Inset: magnified view of the data showing the enhancement of $\alpha_1\text{-N}_2$ and appearance of $\alpha_2\text{-N}_2$ with increasing potassium precoverages.

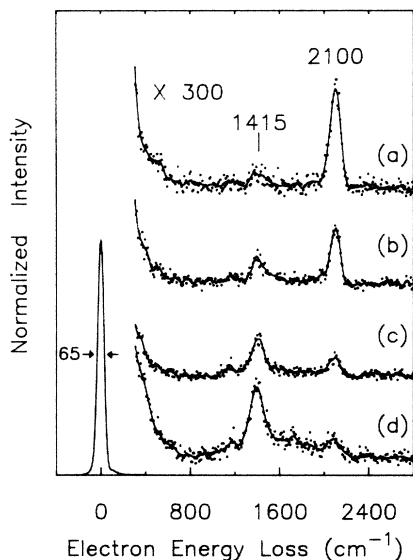


FIG. 3. HREELS data for Fe(111) at 74 K exposed to 10×10^{-6} Torr \cdot s of $^{15}\text{N}_2$ with (curve *a*) an initially clean surface, and surfaces precovered with (curve *b*) 0.04 ± 0.02 , (curve *c*) 0.11 ± 0.02 , and (curve *d*) 0.16 ± 0.05 ML potassium. The addition of potassium results in an enhancement of $\alpha_1\text{-N}_2$, the precursor to dissociation. The additional features observed at the higher potassium coverages are attributed to local K- N_2 interactions.

desorption peak denoted α_2 .^{9,10} Since the α state was not saturated on the unpromoted surface under these conditions, 0.29 ML can be considered a lower bound on the α_1 coverage attainable with a 0.16-ML precoverage of K. The area of the α_2 TDS peak, which increases linearly with K coverage,⁹ was used to determine the K coverage, with the 0.11-ML K-coverage TDS spectrum taken as reference.

The HREELS spectra (Fig. 3) show a corresponding (5.6 ± 1.6) -fold enhancement of the α_1 N-N stretch intensity, demonstrating that the TDS results are representative of the steady-state adsorbate coverage and are not due to interstate conversion during the temperature ramp. This was confirmed by a Monte Carlo simulation of the desorption kinetics, which revealed that the amount of $\alpha_1\text{-N}_2$ that desorbs is within $\approx 20\%$ of the pre-TDS surface coverage.¹² However, in analogy with experiments performed on the unpromoted surface (Fig. 1), HREELS spectra for some K-precovered surfaces were recorded following a temporary temperature increase to 110 K, and the intensity of the α_1 N-N stretch was observed to increase in every case. This indicates that, like the unpromoted surface, the K-precovered surfaces did not reach equilibrium within the duration of the experiment.

As the K precoverage is increased, the small peak that grows in at 1170 cm^{-1} is attributed to the N-N stretch of the α_2 state, as verified by isotope-shift and

heating experiments.¹² This state results from local interactions with the K,¹² and will not be discussed here. Similarly, the broad region of intensity between the α and γ peaks shown in Fig. 3, curve *d*, which becomes more prominent at higher K coverages, is also attributed to short-range K- N_2 interactions.¹²

The increase in the α_1 coverage beyond the saturation coverage for the clean surface is evidence that K adsorption has a long-range, nonkinetic effect. The adsorption of $\alpha\text{-N}_2$ on clean Fe(111) is unusual in that a maximum of 0.10 ± 0.03 ML adsorbs on the surface under equilibrium conditions,⁶ which is small compared with other molecular adsorption systems. Saturation at such a dilute coverage, where adsorbate-adsorbate interactions are expected to be small, indicates the occurrence of strong through-metal repulsive interactions. Adsorbed K apparently reduces these interactions, enabling the substantial increase in α_1 coverage, though no definitive explanation for this effect can be given from our data.

The results indicate that low precoverages of K cause an increase in the sticking coefficient of the π -bonded α_1 state, as is evident from the increase in $\alpha_1\text{-N}_2$ coverage obtained with identical exposures and data acquisition times. To our knowledge, this is the first *direct* observation of alkali-metal-promoted production of a known dissociation precursor. We propose that precoverage with K lowers the barrier for conversion from the γ state to the α_1 state. The barrier may be lowered locally by the lower surface potential surrounding a K atom.¹⁶⁻¹⁸ However, if such a $\gamma\text{-N}_2\text{-K}$ interaction does occur, it must result in the rapid conversion of the perturbed γ to the α_1 state, as no perturbed γ state is observed. In addition, as there is much more α_1 created than α_2 , most of the π -bonded N_2 that results from this conversion must be far enough away from a K atom (i.e., next-nearest neighbor) to remain unperturbed. Alternatively, the barrier may be decreased over a long range by such nonlocal effects as increases in the surface electron density or density of states.¹⁹ Any long-range changes must be subtle, however, as we do not observe significant downshifts ($>20 \text{ cm}^{-1}$) in either the α_1 or γ N-N stretch frequencies.

Promotion of the initial molecular adsorption stages by low coverages of potassium is an important new result, as K promotion of surface reactions has been previously attributed to bond weakening in the dissociation precursor.²⁰ Although the mechanism of promotion of the α_1 adsorption channel is uncertain, the lack of significant shifts in the α_1 and γ N-N stretch frequencies indicates that the N-N bonding of the remaining α_1 - and $\gamma\text{-N}_2$ is not appreciably affected by the coadsorbed K.

For the $\text{N}_2/\text{Fe}(111)$ system the kinetic parameters determined on the K-free surface at low temperatures

(<120 K), where molecular adsorption occurs, accurately describe the dissociative adsorption rate at higher temperatures (>400 K).⁶ Using simple first-order rate equations, we have calculated¹² that lowering the γ - to α_1 -N₂ barrier and slightly increasing the α_1 -N₂ adsorption energy leads to an increase in the equilibrium α_1 -N₂ coverage at high temperatures sufficient to account for the increased N₂ dissociation rate observed on K-precovered Fe(111) at the same temperatures.⁹ This is significant, since the high-temperature dissociation kinetics for the K-promoted surface⁹ can be used to determine correctly the ammonia synthesis rate in a catalytic reactor under industrial conditions.¹ The increased dissociation rate on the K-precovered surface has previously been attributed solely to a more rapid dissociation of the strongly perturbed α_2 -N₂.⁹ While conversion of α_1 - to α_2 -N₂ at temperatures above 74 K might further enhance the overall N₂ dissociation rate, we believe that it would not make a significant contribution.

In conclusion, the vibrational spectrum of γ -N₂ adsorbed on Fe(111) is reported for the first time, identifying this species as terminally bonded N₂. The effects of K on γ - and α -N₂, the dissociation precursor, have also been observed, with unexpected results. We propose that for submonolayer precoverages of K at 74 K, under UHV conditions, γ -N₂-K interactions cause a decrease in the activation barrier for conversion from the terminally bonded γ state to the π -bonded α_1 state, observed as a dramatic enhancement in the sticking coefficient of α_1 -N₂. Furthermore, the maximum coverage of α_1 -N₂ is increased by coadsorption with K. The change in the adsorption-desorption kinetics implied from our results is sufficient to account for the increased N₂ dissociation rate observed at higher temperatures with comparable K precoverages.^{9,12} As the catalytic effects of K have been previously attributed to bond weakening in the dissociation precursor, an increase in the precursor coverage, without significant bond weakening, is a new mechanism for K promotion of surface reactions.

Support of this work by the National Science Foundation-Solid State Chemistry Grant No. DMR-8413561, the Research Corporation, and the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich

No. 6) is gratefully acknowledged. The authors would like to thank Lee J. Richter and Bruce A. Gurney for stimulating discussions, and Joseph A. Stroschio for assistance in the early stages of the experiment.

¹P. Stoltze and J. K. Nørskov, Phys. Rev. Lett. **55**, 2502 (1985).

²G. Ertl, J. Vac. Sci. Technol. A **1**, 1247 (1983).

³F. Bozso, G. Ertl, M. Grunze, and M. Weiss, J. Catal. **49**, 18 (1977), and **50**, 519 (1977).

⁴N. D. Spencer, R. C. Schoonmaker, and G. A. Somorjai, J. Catal. **74**, 129 (1982).

⁵G. Ertl, *Critical Reviews in Solid State and Materials Science* (CRC Press, Boca Raton, Fla., 1982), p. 349, and references therein.

⁶M. Grunze, M. Golze, J. Fuhler, M. Neumann, and E. Schwarz, in *Proceedings of the Eighth International Congress on Catalysis, West Berlin, Germany, 1984* (Verlag-Chemie, Weinheim, West Germany, 1984), p. IV-133.

⁷G. Strasser, M. Grunze, and M. Golze, to be published.

⁸M. Grunze, M. Golze, W. Hirschwald, H.-J. Freund, H. Pulm, U. Seip, M. C. Tsai, G. Ertl, and J. Küppers, Phys. Rev. Lett. **53**, 850 (1984).

⁹G. Ertl, S. B. Lee, and M. Weiss, Surf. Sci. **114**, 527 (1982).

¹⁰M.-C. Tsai, U. Seip, I. C. Bassignana, J. Küppers, and G. Ertl, Surf. Sci. **155**, 387 (1985).

¹¹G. Ertl, S. B. Lee, and M. Weiss, Surf. Sci. **114**, 515 (1982).

¹²L. J. Whitman, C. E. Bartosch, and W. Ho, to be published.

¹³S. B. Lee, M. Weiss, and G. Ertl, Surf. Sci. **108**, 357 (1981).

¹⁴H. Ibach and D. L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations* (Academic, New York, 1982), Chap. 6.

¹⁵C. E. Bartosch, L. J. Whitman, and W. Ho, to be published.

¹⁶H. S. Luftman and J. M. White, Surf. Sci. **139**, 369 (1984).

¹⁷N. D. Lang, S. Holloway, and J. K. Nørskov, Surf. Sci. **150**, 24 (1985).

¹⁸J. Lee, C. P. Hanrahan, J. Arias, R. M. Martin, and H. Metiu, Surf. Sci. **161**, L543 (1985).

¹⁹P. J. Feibelman and D. R. Hamann, Surf. Sci. **149**, 48 (1985).

²⁰H. P. Bonzel, J. Vac. Sci. Technol. A **2**, 866 (1984), and references therein.