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A remarkable heavy atom isotope effect in the dissociative chemisorption of nitrogen on Ru(001)

L. Romm, O. Citri, R. Kosloff, and M. Asscher[a)]
Department of Physical Chemistry and The Fritz Haber and Farkas Research Centers, The Hebrew University, Jerusalem 91904, Israel

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An extremely large isotope effect $[I_{\mathrm{eff}}=P_{\mathrm{diss}}(^{15}N_2)/P_{\mathrm{diss}}(^{14}N_2)]$, has been measured in the dissociative chemisorption of nitrogen molecules over Ru(001). It varies from unity at kinetic energies above 2 eV to 0.2 at $E_k=1.4$ eV. These observations are consistent with a barrier for direct dissociation of 1.8 eV, in agreement with previous experiments and recent *ab initio* density functional theory calculations. It supports earlier studies that proposed tunneling as the dissociation dynamics mechanism. © *2000 American Institute of Physics.* [S0021-9606(00)71119-6]

The rate-limiting step of the heterogeneous catalytic ammonia synthesis from its elements is the dissociative chemisorption of nitrogen on top of an iron-based catalyst.[1,2] The high N–N bond energy of 9.78 eV excludes a direct thermal dissociation process. The catalytic mechanism is therefore based on simultaneous molecular dissociation and the formation of two weaker nitrogen–iron bonds. The microscopic mechanism that governs the dissociation is still open and under discussion. The question is whether a direct dissociation mechanism takes place or one that involves a molecular intermediate, in which the nitrogen triple bond is weakened.

The most active noniron catalyst for ammonia synthesis is ruthenium,[3(a)] the subject of the present report, which only recently became an industrial catalyst. Consequently, the number of studies of this system has rapidly increased in recent years.[3,4] The dominant role of steps in the dissociation of *thermal* N_2 on Ru(001) has recently been demonstrated.[5] It was suggested that the weakly adsorbed nitrogen molecules need to migrate from their impact position to the nearby step in order to dissociate.

A direct dissociation in which a nitrogen molecule approaching from the gas phase fragments on impact, is an alternative mechanism, in particular for the more energetic molecules.[5,6,8,9] It implies that dynamical variables such as the collision energy and the initial vibrational state should strongly influence the dissociation probability (P_{diss}).

Evidence for this possibility has been shown in molecular beam surface scattering studies. Orders of magnitude enhancement of P_{diss} was observed upon the increase of incident kinetic energy for N_2/Fe(111),[7] N_2/Re(001),[8] and N_2/Ru(001),[9] including the effect of vibration.[7–10] At higher kinetic energies of the colliders, the crystal temperature has only a marginal influence on the process.[9–11] A kinetic scheme based on the direct dissociation approach has thus been introduced without the involvement of an intermediate molecular nitrogen state, which nicely reproduced the measured rate of ammonia synthesis over iron catalysts.[12–14]

A dynamical model rationalizing the experimental results employs a nonadiabatic picture in which molecular nitrogen from the gas phase switches its electronic structure upon impact to an adsorbed atomic nitrogen.[6,8–10] The lowest energy point on the crossing seam between the molecular and atomic potentials is located at 1.8 eV above the zero gas phase energy for the N_2/Ru system.[9] Based on this model, the dissociation has to proceed via a *tunneling* mechanism at incident energies below this crossing point. A minimum barrier of similar magnitude (≈2 eV) was recently computed for the dissociation of N_2 on Ru(001) (a fully relaxed system) using density functional theory.[15(a)] This is an improved value compared to an earlier study that suggested a barrier of 1.35 eV.[15(b)] The important role of vibrational excitation of the impinging N_2 molecules in enhancing its dissociative chemisorption rate was indicated in Ref. 15(a), confirming an earlier study.[9] This was deduced from an observation of vibrational population inversion in the recombinative desorption of nitrogen molecules from Ru(001).

The most significant theoretical prediction of the tunneling mechanism is that a measurable dynamical isotope effect should be observed. The dissociation of the lighter $^{14}N_2$ isotope should be enhanced significantly relative to the heavier $^{15}N_2$ for incident kinetic energies below the crossing seam, where deep tunneling takes place. At collision energies above the crossing seam the isotope effect should vanish.[6,8–10] This major element of the theoretical model has never been tested experimentally.

In order to address the isotope effect hypothesis and in particular its kinetic energy dependence, isotopic substitution has been introduced as a new experimental-dynamical variable for this system. Employing supersonic molecular beam techniques, the two nitrogen isotopes $^{14}N_2$ and $^{15}N_2$ seeded in hydrogen were accelerated onto a Ru(001) single-crystal surface and their dissociation has been studied as a function of incident kinetic energy.

The experiments reported here were conducted in a molecular beam-ultrahigh vacuum (UHV) scattering system.[9,16] The supersonic nitrogen beam was generated in a triply differentially pumped section, where N_2 kinetic energy was controlled by seeding in hydrogen or helium and by varying

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[a)] Electronic mail: asscher@batata.fh.huji.ac.il

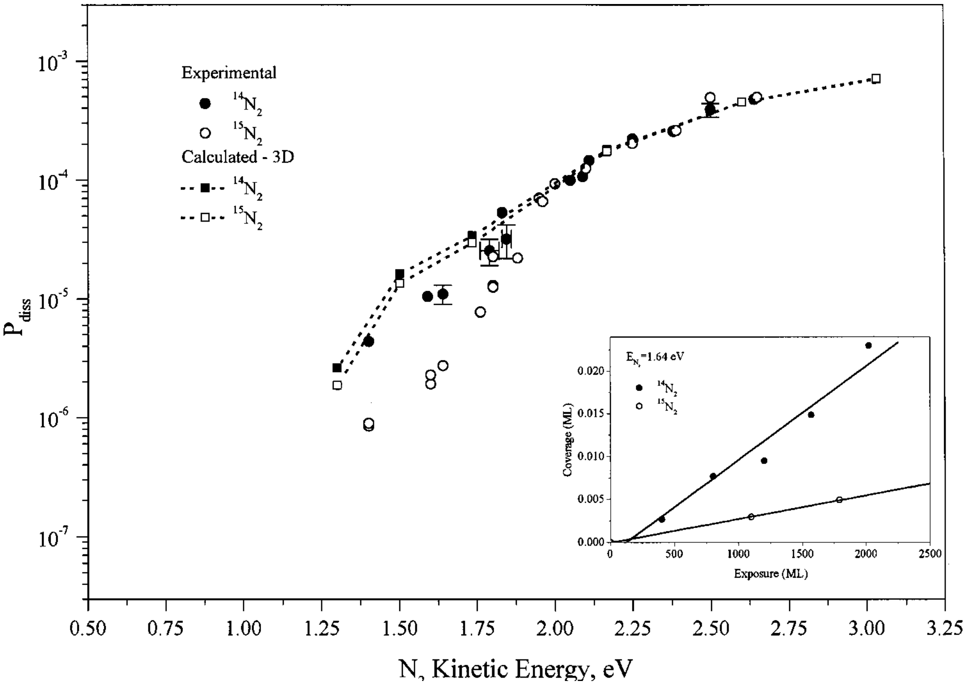

FIG. 1. The dissociation probability of $^{15}N_2$ and $^{14}N_2$ on Ru(001) at 600 K as a function of incident kinetic energy at normal angle of incidence. The inset shows typical coverage versus exposure curves which are used to construct the experimental P_{diss}. The calculated points were obtained by the time-dependent wave-packet calculations, see the text and Ref. 9.

the nozzle temperature. The incident kinetic energy was determined by a time of flight instrument. A miniature 400 Hz chopper defined the initial flight time to the ionizers of two separate quadrupole mass spectrometers. The first has a crossed-beam ionizer located before the sample while the second was at an on-axis configuration behind the sample. This setup improved the accuracy of the nitrogen molecules flight time measurements and thus our determination of incident kinetic energies. Kinetic energy distributions were characterized by $\Delta E/E = 0.25$ at nozzle temperature $T_n = 300$ K, which increased to 0.35 at $T_n = 1000$ K. Dissociation probability measurements of $^{14}N_2$ were independent of the nozzle material made either of hard Al_2O_3 (Ref. 9) or from Mo tubes. In the present study only Mo nozzles were used. All measurements reported here were performed at normal angle of incidence.

The UHV chamber had a typical base pressure of 2×10^{-10} Torr, rising to 4×10^{-8} Torr when the beam is on. The sample was prepared and cleaned by both sputter annealing and oxygen treatment, showing afterwards a very sharp hexagonal low energy electron diffraction pattern. Two Ru crystals from different sources, cut to within 0.5° of the (001) crystallographic plane, were used during the course of this study. The results obtained from these two crystals scatter within the experimental uncertainty. Nitrogen flux was $(1.5 \pm 0.5) \times 10^{14}$ molecules/cm^2 s. All nitrogen dissociation studies were performed at fixed crystal temperature of 600 K to avoid any background gas adsorption.[9] The dissociation yield of the impinging nitrogen molecules has been determined by integrating the area under the temperature programmed desorption (TPD) signal of the recombinative desorption peak at mass 14/15, near 950 K at a heating rate of 12 K/s. This method is sensitive to atomic nitrogen coverages down to 0.001 of a monolayer. All filaments were shut off during the beam exposure time to avoid ammonia production at the hot filaments,[9,11] which would add to the population of nitrogen atoms on the surface.

Two gas mixtures were used: One having 1%–3% $^{15}N_2$ in H_2 ($^{15}N_2$ from Isotech, 99.0±0.15% atom purity, impurities were $^{15}N_2O$ and ^{15}NO) and the other mixture was of $^{14}N_2$ (99.9999% purity) also in H_2. The mixtures were further purified by flowing through a 2.5 m liquid nitrogen trap, after 24 h mixing time in 50 l gas bottles at total pressure of 6 atm. We have repeated some of these measurements with up to three such traps (total of 7.5 m copper tubing immersed in liquid nitrogen) in order to further check the level of cleanliness of the gases in the beam. Identical results were obtained with one or three traps. Another precaution was taken to avoid the rare possibility of surface chemistry on the surface of the molybdenum nozzle that may affect our measurements. By slightly varying the degree of seeding of both isotopes of nitrogen in hydrogen and changing the nozzle temperature in the range 650–850 K, the catalytic activity of the nozzle should have changed. The measured isotope effect in the energy range shown in Fig. 2 was insensitive to these parameters.

The data points shown in Fig. 1 were obtained from the slopes of coverage versus exposure curves. A linear relation between nitrogen coverage and its exposure up to coverages of more than 8% of a monolayer indicates that dissociation occurs predominantly on terraces in a direct collision event, which means that defects do not significantly contribute. These results are consistent with Ref. 5, implying a direct dissociation mechanism at the higher kinetic energies ($E_k > 1.4$ eV). The data points in Fig. 1 are the result of up to three coverage versus exposure points for the $^{15}N_2$ experiments and up to six points in the case of $^{14}N_2$. The low sticking probabilities at energies below 1.4 eV resulted in nonreproducible measurements. At this point, therefore, we limit our quantitative discussion to energies above 1.4 eV.

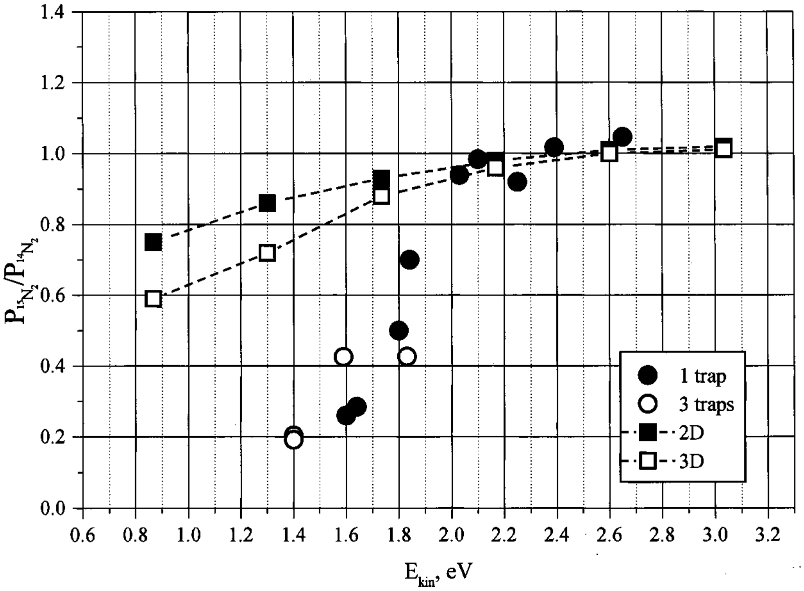

FIG. 2. The measured and calculated isotope effect as a function of incident kinetic energy. Unlike the three-dimensional calculations, the two-dimensional results do not include surface recoil.

Moreover, recent measurements suggest that there is a significant contribution to our TPD from bulk nitrogen atoms at extremely low coverages[17] which may limit the accuracy of our low energy data.

In Fig. 1 the measured dissociative sticking probabilities ($P_{\rm diss}$) are presented for $^{14}N_2$ and $^{15}N_2$ as a function of incident kinetic energy at normal angle of incidence. The data points of $P_{\rm diss}(^{15}N_2)$ and $P_{\rm diss}(^{14}N_2)$ practically overlap for energies above 2 eV. Below this value, they start to split, where the heavier isotope has a lower dissociation probability as the energy decreases. A summary of all the measured values of the isotope effect $I_{\rm eff}=P_{\rm diss}(^{15}N_2)/P_{\rm diss}(^{14}N_2)$ as a function of incidence energy is shown in Fig. 2. $I_{\rm eff}$ changes from unity for kinetic energies above 2 eV, monotonically dropping to 0.2 at 1.4 eV.

A common model to explain an isotope effect while crossing a barrier is based on a one-dimensional semiclassical tunneling formula:[18]

$$P_{\rm diss}\approx P_0\exp\left(-2\frac{\sqrt{2M}}{\hbar}\int_a^b \sqrt{[V(q)-E]}\,dq\right) \qquad (E<V_T), \tag{1}$$

where P_0 is the dissociation probability at the top of the barrier ($E=V_T$), M is the mass of the tunneling particle, the integral limits a, b are the borders of the classically forbidden region, and q the tunneling coordinate. In the case of the N_2/Ru(001) system $P_0\approx 10^{-2}$.

Since the integral representing the area under the barrier should be mass independent,[18] the isotope ratio is directly related to the dissociation probability:

$$I_{\rm eff}(E)=\frac{P_{\rm diss}(^{15}N_2)}{P_{\rm diss}(^{14}N_2)}=\left(\frac{P_{\rm diss}(E)}{P_0}\right)^{\eta}, \tag{2}$$

where $P_{\rm diss}(E)$ is $P_{\rm diss}(^{15}N_2)$ at incident kinetic energy E and the mass-dependent exponent is $\eta=(1-\sqrt{M_{14}/M_{15}})$. The presence of the mass ratio at the exponent offers an explanation for strong sensitivity to the mass of the dissociating molecule.

The exponent η in the semiclassical model underestimates the experimentally observed isotope effect shown in Fig. 2. The full quantum nonadiabatic model calculations[9] predict higher exponent, nevertheless it also underestimates the measured values (see Fig. 2).

Searching for alternative reasons for the observed dynamical isotope effect, a zero point energy explanation can be eliminated. Its maximum value of 0.83 for the N_2/Ru system is way below the experimental values and is not energy dependent. Tunneling under a single adiabatic potential energy surface can in principle explain isotope effect but it is always smaller than a nonadiabatic approach for the same potentials.

To conclude, a very large isotope effect has been reported here for nitrogen dissociation on Ru(001), for the first time, as a function of incident kinetic energy of the colliding nitrogen molecules. Model calculations based on tunneling through a large barrier for dissociation of 1.8 eV qualitatively explain the results. In particular, the model predicts correctly the onset of the isotope effect at energies just below the barrier. This model, however, fails to explain the actual magnitude of the isotope effect as determined experimentally. This might be due to a limited number of nuclear degrees of freedom (molecular and substrate related) used in the model or because of the involvement of additional excited electronic states.

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[1] F. Haber, Z. Elektrochem. Angew. Phys. Chem. **16**, 244 (1910); **20**, 597 (1914).

[2] (a) G. Ertl, in *Catalytic Ammonia Synthesis*, edited by J. R. Jennings (Plenum, New York, 1991); p. 109, and references therein; (a) E. Christoffersen, J. J. Mortensen, P. Stoltze, and J. K. Nørskov, Isr. J. Chem. **38**, 279 (1999).

[3] (a) K.-I. Aika and K. Tamura, in *Ammonia—Catalysis and Manufacture*, edited by A. Nielsen (Springer, Berlin, 1995), Chap. 3, p. 103; (b) D. C. Papageorgopoulos, B. Berendek, M. Verwoest, B. Riedmuller, S. Stolte, and A. W. Kleyn, Chem. Phys. Lett. **305**, 401 (1999); (c) L. Diekhoner, A.

Baurichter, H. Mortensen, and A. C. Luntz, J. Chem. Phys. **112**, 2507 (2000).

[4] K. Jacobi, Phys. Status Solidi A **177**, 37 (2000).

[5] S. Dahl, A. Logadottir, R. C. Egeberg, J. H. Larsen, I. Chorkendorff, E. Tornquist, and J. K. Nørskov, Phys. Rev. Lett. **83**, 1814 (1999).

[6] G. Haase, M. Asscher, and R. Kosloff, J. Chem. Phys. **90**, 3346 (1989).

[7] C. T. Rettner and H. Stein, Phys. Rev. Lett. **59**, 2768 (1987); H. Stein and C. T. Rettner, J. Chem. Phys. **87**, 770 (1987).

[8] E. Por, G. Haase, O. Citri, R. Kosloff, and M. Asscher, Chem. Phys. Lett. **188**, 553 (1991).

[9] L. Romm, G. Katz, R. Kosloff, and M. Asscher, J. Phys. Chem. B **101**, 2213 (1997).

[10] G. Katz and R. Kosloff, J. Chem. Phys. **103**, 9475 (1995).

[11] (a) H. Shi, K. Jacobi, and G. Ertl, J. Chem. Phys. **99**, 9248 (1993); (b) H. Dietrich, P. Geng, K. Jacobi, and G. Ertl, *ibid.* **104**, 375 (1996).

[12] F. Y. Hansen, N. E. Henriksen, and G. D. Billing, Surf. Sci. **324**, 55 (1995).

[13] G. D. Billing, A. Guldberg, N. E. Henriksen, and F. Y. Hansen, Chem. Phys. **147**, 1 (1990).

[14] N. E. Henriksen, G. D. Billing, and F. Y. Hansen, Surf. Sci. **227**, 224 (1990).

[15] (a) M. J. Murphy, J. F. Skelly, A. Hodgson, and B. Hammer, J. Chem. Phys. **110**, 6954 (1999); (b) J. J. Mortensen, Y. Morikawa, B. Hammer, and J. K. Nørskov, J. Catal. **169**, 85 (1997).

[16] L. Romm, Y. Zeiri, and M. Asscher, J. Chem. Phys. **108**, 8605 (1998).

[17] Y. Lilach, S. Danziger, and M. Asscher (unpublished).

[18] H. Nakamura, J. Chem. Phys. **87**, 4031 (1987).