Nonstandard Behavior of a Negative Ion Reaction at Very Low Temperatures

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We have studied the negative ion reaction $NH_2^- + H_2 \rightarrow NH_3 + H^-$ in the temperature range from 300 to 8 K. We observe a strongly suppressed probability for proton transfer at room temperature. With decreasing temperature, this probability increases, in accordance with a longer lifetime of an intermediate anion-neutral complex. At low temperatures, a maximum in the reaction rate coefficient is observed that suggests the presence of a very small barrier at long range or a quantum mechanical resonance feature.

Ion-molecule reactions play a vital role in such widely diverse areas as biological signal processing, organic chemistry, plasma physics, or reaction chains in Earth's ionosphere. In the interstellar medium, the rich chemistry of ion-molecule reactions plays a key role in the formation of larger organic molecules in space [1], which might be the building blocks of life. Several new methods are currently emerging to study cold molecular ions [2–4] and low-energy ion-molecule reactions [5–7]. At low temperatures, such investigations are almost exclusively restricted to cations. An exception is the nucleophilic substitution (S_N2) reaction $Cl^- + CH_3Br$ forming $ClCH_3 + Br^-$, which was studied down to 23 K of translational and internal temperature [8], until now the lowest temperature for an anion-molecule reaction experiment. That experiment showed an increase in the rate coefficient by orders of magnitude, which is explained by an increased lifetime of an intermediate reaction complex with lower temperature. Studies on the ternary rate coefficient of a symmetric S_N2 reaction could confirm such an inverse temperature dependence of the lifetime of an intermediate complex [9]. Laboratory studies on the reactivity of negative ions at low temperatures are becoming exceedingly important for modeling the abundance of negative ions in the interstellar medium, where several species have recently been observed for the first time [10,11], and for understanding their role in the evolution of these cold interstellar environments.

Proton transfer reactions between ions and small molecules are fast and proceed at or near the collision rate when exoergic. The essentially unit probability has made cationic proton transfer the ideal benchmark system for the development of ion-molecule collision rate theories [12]. Few systems with unusually low rate coefficients, however, have attracted attention. For cations, such effects were observed for large reactants such as pyridines and amines and are attributed to steric hindrance [13]. For proton transfer to anions, in contrast, slow kinetics are assumed to have a different cause. As first suggested by Farneth and Brauman [14], their potential energy surface exhibits a double minimum structure. The reaction efficiency is

then reduced due to the low density of states at the transition state, which represents a dynamical "bottleneck" for the reaction. In proton transfer processes requiring spin conversion, an additional "spin barrier" has been found [15].

One of the simplest proton transfer reactions involving anions is that of the amino radical anion NH_2^- with hydrogen

$$NH_2^- + H_2 \rightarrow NH_3 + H^-, \tag{1}$$
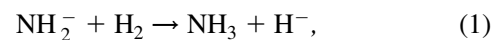
which is slightly exoergic by about 140 meV. A rate coefficient of this reaction has been measured at room temperature [16] and found to be about 2 orders of magnitude below the capture limit. *Ab initio* calculations [17] show that reaction (1) proceeds along a double well potential separated by a barrier which, however, is lower in energy than the free reactants (see Fig. 1). Trajectory calculations on S_N2 reactions, which exhibit similar double well structures, attribute the dynamical hindrance to inefficient coupling of the different vibrational degrees of freedom in the entrance channel complex [18]. Such reactions can be treated in a three-step process [14]. In the first
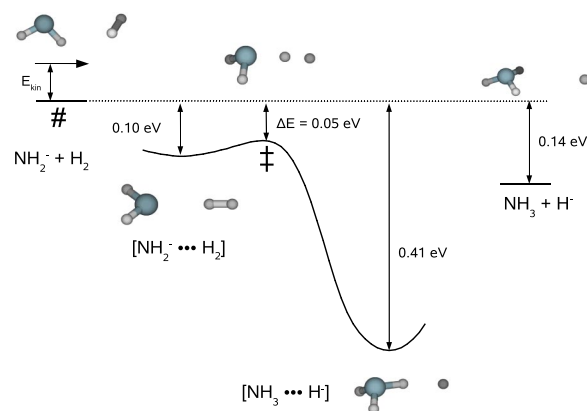

FIG. 1 (color online). *Ab initio* calculated minimum energy pathway of the reaction $NH_2^- + H_2 \rightarrow NH_3 + H^-$ [23]. All energies have been corrected for their vibrational zero point energies [26].

step, the reactant particles, here NH_2^- and H_2, form a metastable collision complex $[NH_2^- \cdots H_2]$. At the central barrier, the saddle point for the molecular rearrangement is reached which leads to the transfer of a proton from the H_2 molecule to the amino radical anion NH_2^-. In this way, a highly excited ammonia-hydride complex $[NH_3 \cdots H^-]$ is formed in the second step, which finally decays into the products.

In this Letter, we investigate the proton transfer reaction (1) as a model system for low-temperature reaction dynamics on a complex potential energy surface. We obtain its rate coefficient in the temperature range between 300 and 8 K. The rate coefficient shows an inverse temperature dependence from 300 to 20 K, where it reaches a maximum. Subsequently, the rate coefficient drops as one goes to even lower temperatures. Modeling the rate coefficient with statistical theories supported by *ab initio* calculations allows us to understand the inverse temperature behavior of the system down to 20 K but not the drop in reaction rate at lower temperature.

The experiment is carried out in a 22-pole radio-frequency ion trap, which has been described in Refs. [19,20]. The trap consists of a cylindrical structure of 22 rods, planted alternatingly into two side plates and connected to the two opposite phases of a radio-frequency oscillator running at 8 MHz. While this provides the radial confinement, dc voltages of 2 V applied to entrance and exit electrodes lead to trapping along the axial direction. The trapped ions thermalize via collisions with helium buffer gas, which is applied into the housing of the trap at well-defined densities of typically $n_{He} = 5 \times 10^{14}$ cm^{-3}. The trap temperature is variable in the temperature range between 8 and 300 K.

NH_2^- anions are produced in a separate ion source by dissociative attachment of secondary electrons to NH_3 in a supersonic expansion of 10% ammonia and 90% argon counterpropagated by a 1 keV electron beam:

$$NH_3 + e^- \rightarrow (NH_3^-)^* \rightarrow NH_2^- + H. \qquad (2)$$
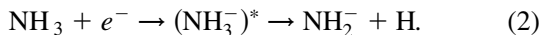
Reaction (1) is induced for the trapped NH_2^- anions by adding molecular hydrogen gas to the helium buffer gas in the ion trap via a precision leak valve. The absolute hydrogen density inside the trap is obtained by measuring the hydrogen pressure with a capacitance pressure gauge. After variable interaction times of the stored ions with the reactant gas, the trap is emptied, and the mass-resolved intensity of the stored ions is measured using a time-of-flight spectrometer. The time-dependent decay of the NH_2^- intensity is fitted to yield the reaction rate. H^- product ions cannot be trapped in the multipole trap at the employed rf frequency and therefore are not detected. No cluster formation is observed even at low temperatures. At temperatures above 150 K, a parasitic proton transfer reaction with H_2O impurities is observed through the appearance of OH^- ions in the trap. Here the decay of the NH_2^- ions is fitted with a rate equation model that includes the reaction

with water. This yields a correction of up to 10% for the partial decay rate with respect to reactions with hydrogen molecules. To obtain precise values of the reaction rate coefficient, the decay rate of the NH_2^- anions is measured as a function of the hydrogen density in the 22-pole trap for 8 and 300 K (see Fig. 2). The linear dependence and the interception of the origin confirm that the anions undergo reactions with hydrogen and not with any further impurities in the buffer gas. It has been verified that the decay rate does not depend on the density of the helium buffer gas.

The reaction rate coefficients are obtained by fitting the slopes in Fig. 2. We obtain $k_{300 \text{ K}} = 0.025(1) \times 10^{-9}$ cm^3/s $= 0.016(1) \times k_{\text{Langevin}}$ and $k_{8 \text{ K}} = 0.129(3) \times 10^{-9}$ cm^3/s $= 0.081(2) \times k_{\text{Langevin}}$ for the two temperatures. The capture-limited Langevin rate is calculated to be $k_{\text{Langevin}} = e/(2\epsilon_0)\sqrt{\alpha/\mu} = 1.59 \times 10^{-9}$ cm^3/s, where α is the H_2 polarizability and μ the reduced mass of the collision system [21]. The accuracy of the rate coefficients is estimated from the statistical accuracy of the χ^2 fit based on the statistical errors of the individual decay rate measurements. We find excellent agreement at a fivefold improved accuracy of our 300 K measurement with the previous value $0.023(5) \times 10^{-9}$ cm^3/s $= 0.014(3) \times k_{\text{Langevin}}$ of Ref. [16]. The data show that at room temperature reaction (1) proceeds only at a fraction of the Langevin rate, its maximum possible reaction rate. As discussed below, this indicates that dynamical constraints hinder the system to form products. For the reaction rate coefficient at 8 K, we obtain a much higher value. Thus, the removal of translational and rotational energy increases the chances of forming products.

For comparison, we have investigated the reaction with deuterium molecules

$$NH_2^- + D_2 \rightarrow NH_2D + D^-. \qquad (3)$$

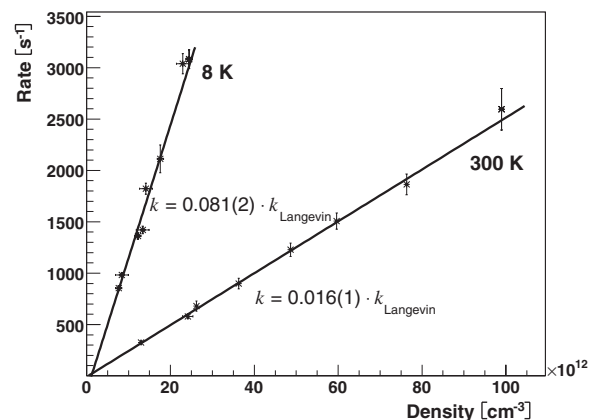Since the electronic potential surface is untouched in this

FIG. 2. Measurement of the loss rate of NH_2^- ions due to proton transfer as a function of the H_2 number density n_{H_2} in the 22-pole trap. The value at 300 K compares well to the only previous measurement of $0.014(3) \times k_{\text{Langevin}}$ [16], with $k_{\text{Langevin}} = 1.59 \times 10^{-9}$ cm^3 s^{-1}.

case, any isotope effects in the reaction efficiency may provide further insight into the atomic dynamics on the potential surface. The measured rate coefficients for the deuterated reaction are significantly lower than for the hydrogen system, for both 300 and 8 K, with the 8 K value again larger than the 300 K value. The relative change is given by ratios $k_{D_2}/k_{H_2} = (39 \pm 3)\%$ at 300 K and $k_{D_2}/k_{H_2} = (58 \pm 5)\%$ at 8 K, respectively. Both ratios are smaller than would be expected from the ratio of the Langevin rate coefficients of 74%, which points to an enhanced dynamical suppression of the reaction with D_2 compared to H_2.

In order to clarify the influence of the temperature on the dynamics of reaction (1) and (3), we measure the reaction rate coefficient over the entire temperature range from 8 to 300 K. For this purpose we employ a more efficient scheme by measuring the NH_2^- decay rate at a fixed, stable hydrogen density at the pressure gauge for different temperatures. The data sets are then normalized to the 8 or 300 K rate coefficients. In Fig. 3, the reaction probabilities, defined as the measured rate coefficient divided by the temperature-independent Langevin rate coefficient, are plotted. For both hydrogen and deuterium, the data show a strong increase of the rate coefficient with decreasing temperature. At 20 (15) K, the rate coefficient peaks at a maximum near 10% reaction probability, which is a factor of 7 (11) higher for H_2 (D_2), as compared to room temperature. Between 20 and 8 K, however, the rate coefficient is found to decrease again by a factor of 1.4 for both H_2 and D_2. Such a low-temperature effect has not been observed before in anion-molecule reactions.

The observed strong increase in the reaction rate coefficient with decreasing temperature is a feature that is also observed in other ion-molecule reactions [8]. In order to model this inverse temperature dependence, we have performed Rice-Ramsberger-Kassel-Marcus (RRKM) and
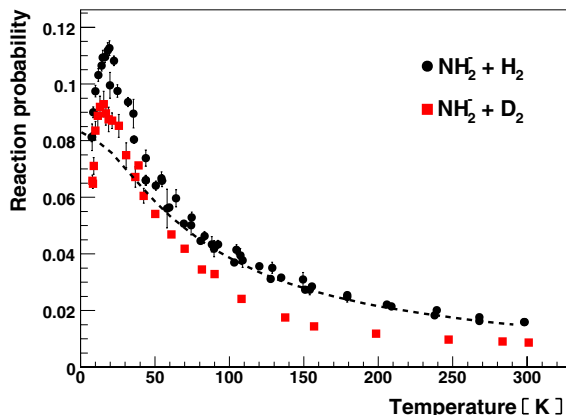

FIG. 3 (color online). Reaction probability, defined as the ratio $k/k_{Langevin}$, for $NH_2^- + H_2$ and $NH_2^- + D_2$ as a function of temperature. The dashed line shows the phase space theory calculation of the reaction with H_2, which is based on a capture rate that is scaled down by a factor of 12 from the Langevin rate to match the measured value at 300 K.

phase space theory calculations [22] based on energy levels and vibrational frequencies that we calculated using the GAUSSIAN 03 software package [23]. The assumption of the statistical model is that the reaction proceeds via the formation of an entrance channel complex followed by energy randomization and either dissociation back to free reactants or passage via the transition state and formation of the products. To obtain the rate of reaction (1), we use the Langevin model to calculate the formation rate of the $[NH_2^- \cdots H_2]$ complex, the RRKM approach for the unimolecular dissociation of the complex into products, and phase space theory, which also takes into account the conservation of the total angular momentum of the system, for the decay rate of the complex back to the reactants. The rate coefficient is the product of the capture rate $k_{capture}$ for forming the intermediate complex and the branching ratio for the decay to the products

$$k(E_{kin}) = k_{capture} \frac{N^{\ddagger}(E_{kin} + \Delta E)}{N^{\#}(E_{kin}) + N^{\ddagger}(E_{kin} + \Delta E)}. \quad (4)$$

Here $N^{\ddagger}(E_{kin} + \Delta E)$ and $N^{\#}(E_{kin})$ denote the sum of states at the transition state ‡ and the loose transition state # identified with the separated reactants at the centrifugal barrier of the system, respectively. The energies E_{kin} and ΔE are defined according to Fig. 1 as the translational energy of the reactants and the energy difference between the transition states ‡ and #, respectively.

Assuming that the Langevin rate coefficient describes the formation rate of the complex, the statistical model yields a 300 K reaction rate coefficient that is an order of magnitude higher than the experimental result. The capture rate was therefore scaled down by a factor of 12 to match the measured value at 300 K, which is plausible in terms of a steric hindrance factor that influences the formation of the entrance channel complex. It is not contradictive that the reaction shows statistical behavior after the system has overcome the initial dynamical bottlenecks [24]. The calculated temperature-dependent rate coefficient for the reaction with H_2 is shown by the dashed line in Fig. 3. The observed inverse temperature dependence of the rate coefficient due to the different energy dependences of the sums of states is also referred to as "channel switching" [25]. Above 100 K, the calculation exhibits a remarkable agreement with the measurement. At lower temperatures, the experimental rate increases faster before it passes its low-temperature maximum.

The temperature dependence of the rate below 100 K is not easily explained. The increase between 8 and 20 K may suggest an Arrhenius-type behavior with an activation energy on the order of 15–20 K. However, the calculation of the energy along the minimum energy path of the potential energy surface [26] shows no indication for an overall barrier on the electronic potential energy surface (see Fig. 1). In the temperature range of the experiment, all electronic and vibrational excitations of NH_2^- and H_2 are

frozen out and thus do not participate in the reaction process. In the current experiment, the rotational level population of H_2 is given by the 3:1 mixture of the ortho ($N = 1$) and para ($N = 0$) states and remains constant in the temperature range below 50 K. Regarding the reactants, only rotational excitation of the NH_2^- anion and orbital angular momentum considerations can therefore play a major role. In the transition state configuration at the central barrier, only two excited vibrational states (at 350 and 500 cm^{-1}) are energetically accessible. This shows that at these low temperatures the assumption of a smooth density of states breaks down, and the discrete quantum mechanical structure of the system has to be taken into account. Consequently, the statistical model, which describes the reaction rate coefficient quite well in the temperature range above 100 K, is not best suited to explain the low-temperature behavior. Instead, isolated scattering resonances, which are found to occur at ultralow temperatures [27], are expected to become important in the studied temperature range due to the light mass of the H and D atoms [28]. Broadened by the thermal distribution of collision energies in the trap, such resonances will lead to maxima in the reaction rate coefficient similar to the one observed in Fig. 3. The small change in the temperature position of the rate coefficient maximum for H_2 and D_2 suggests that the long-range interaction is responsible for the rate coefficient maximum, because at short distances one would expect much larger shifts of eigenenergies due to the change in vibrational level spacing between hydrogen and deuterium. Low-energy quantum scattering calculations are needed to explain the rate coefficient maximum. Furthermore, it will be interesting to clarify the role of the ortho and para components of H_2 in this effect.

In conclusion, we have measured the reaction rate coefficient of the exoergic proton transfer reaction $NH_2^- + H_2 \rightarrow NH_3 + H^-$ and its deuterated analog $NH_2^- + D_2 \rightarrow NH_2D + D^-$ over a range of temperatures from 300 to 8 K. We observe a reaction efficiency that is more than a factor of 10 below the capture limit. The rate coefficient shows an inverse temperature dependence down to 20 K, where it reaches a maximum. The inverse temperature dependence can qualitatively be explained in terms of a statistical model if one assumes a dynamical bottleneck that hinders the formation of intermediate reaction complexes. At low temperatures, however, the quantum nature of the system has to be taken into account. The peaking behavior with the subsequent drop in the reaction probability could point to a reaction resonance. This is an effect that may also be found in other reactions when advancing to low temperatures.

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