Observation of orbiting resonances in He(3S1) + NH3 Penning ionization

Justin Jankunas1, Krzysztof Jachymski2, Michal Hapka3, and Andreas Osterwalder1

1Institute for Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland
2Faculty of Physics, University of Warsaw, Pasteura 5, 02-093 Warsaw, Poland
3Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

(Dated: March 2, 2022)

A merged-beam study of the gas phase He(3S1) + NH3 Penning ionization reaction dynamics in the collision energy range 3.3 μeV < E_{coll} < 10 meV is presented. In this energy range the reaction rate is governed by long-range attraction. Shape resonances are observed at collision energies of 1.8 meV and 7.3 meV and are assigned to ℓ=15,16 and ℓ=20,21 partial waves, respectively. The experimental results, representing the first observation of shape resonances in a collision with a polyatomic molecule, are well reproduced by theoretical calculations with the short-range reaction probability  P_{sr} = 0.035.

Introduction. Chemical reactions of polyatomic molecules at low collision energies are interesting for a number of reasons. Studies of cold molecular collisions are an important source of information for interstellar chemistry. From a fundamental point of view, an important motivation lies in the potential observation of quantum effects in molecular scattering, like quantum state-specific reactivity and scattering resonances [1]. Low energy collisions are characterised by few angular momentum partial waves. A prominent consequence of this is the possible observation of so-called partial-wave resonances, where a single partial wave can dominate the total reaction cross section [1]. In contrast, hundreds or even thousands of partial waves contribute in collisions at thermal energies, and the reaction can be treated statistically [2]. Resonances are among the clearest signatures of the quantum mechanical character of a molecular scattering event. The first observation of orbiting resonances dates back to 1974 when the elastic scattering dynamics of H with Xe was studied [3]. Low-energy scattering was not possible then, but this particular collision system, having a suitable interaction potential and low reduced mass, nevertheless enabled this important observation. Until recently, that paper remained the only report on orbiting resonances in neutral reactions because for other collision systems it was not possible to reach the required temperature range. Two recent developments, the merged beam technique and low-angle crossed beam scattering, have finally enabled scientists to venture into this regime and observe resonances in other reactions as well [4][5].

Studies of scattering resonances to date only targeted collisions involving atoms or diatomic molecules [6][7]. This paper reports the first observation of reactive scattering resonances in Penning Ionization (PI) of a polyatomic molecule with metastable helium. Specifically, the He(3S1) + NH3 PI reaction is investigated in the collision energy (E_{coll}) range 38 mK < E_{coll} < 125 K. In contrast to atoms and diatomic molecules polyatomic molecules have a further reduced symmetry, and allow for a potentially more complex stereochemistry. The enhanced complexity also potentially allows for a larger number of reaction channels, and it is not immediately clear how this affects a possible observation of resonances.

The first experiments on molecular PI were performed as early as 1970s [9], but theoretical treatment of these electron transfer reactions has not been nearly as detailed as for the PI of atoms. PI at low E_{coll} has recently been studied using the merged-beam technique, where excited helium and neon atoms were collided with argon H2 [5][7], ammonia [8][10], CH3F [11], and CHF3 [12] at collision energies as low as 0.8 μeV (9 mK) where fewer than ten partial waves contribute to the collision. Partial wave resonances have been observed in He* + H2/HD/D2/Ar Penning ionization reactions, and were rather well reproduced theoretically [7].

In the present reaction two channels are observed,

\begin{equation}
\text{He}^*(3S_1) + \text{NH}_3 \rightarrow \text{NH}_3^+ + \text{He} + e^- \quad (1)
\end{equation}

\begin{equation}
\text{He}^*(3S_1) + \text{NH}_3 \rightarrow \text{NH}_3^++ \text{H} + \text{He} + e^- \quad (2)
\end{equation}

The internal energy of helium in the first excited 3S1 state is sufficient to ionize NH3 through the ground X state of the ion or through the first excited state, the NH3+ (Â) state, 4.8 eV above the ground state. The Â state is produced by removal of an electron from the lone pair and predominantly in the non-dissociating vibrational ground state [13]. The Â state, on the other hand, is formed by the removal of an electron from one of the N-H bonds and has a high probability to dissociate. Based on this the authors of reference [13] suggest that the branching between the two channels is, in fact, a stereodynamic probe of this reaction. The relative yield of the dissociative ionization (Eq. 2) in the related Ne*(3P2) + NH3 reaction has been observed to be constant over the entire range of collision energies from below 100 mK up to ≈250 K [4]. At higher energies, the branching ratio for dissociative PI in the Ne*+NH3 reaction slightly increases [13].

Experimental setup. The experimental apparatus and procedure is described in detail elsewhere [4]. Briefly, electrostatic and magnetic hexapole guides are used to
merge a beam of He(final state) atoms with a beam of NH3 molecules. Metastable helium atoms are produced in a commercial dielectric barrier discharge [14], mounted directly behind an Even-Lavie pulsed valve [15], operated with a backing pressure of 4 bars. Presumably two metastable helium states are produced, He(3S1) and He(3S1), but only the paramagnetic He(3S1) species is guided, resulting in a very pure beam of atoms. The speed of He(3S1) (denoted He* in the following) beam is controlled by cooling the valve in the range 140 K – 200 K, resulting in continuously tuneable beam speeds in the range 1110 m/s – 1420 m/s. Ammonia is prepared in a pulsed valve (general valve Series 9) with a backing pressure of 1.5 bar. The speed of the ammonia beam is controlled by using pure NH3 or seeding it in Ne or Ar, resulting in beam velocities of approximately 1050 m/s, 820 m/s, or 620 m/s, respectively. In the electrostatic guide only low-field seeking (lfs) states are confined. Of the two states of the ammonia inversion doublet only the upper component is lfs while the lower component is high-field seeking and thus removed entirely from the beam. The He* and NH3 beams are overlapped in space and time in the extraction region of a time-of-flight mass spectrometer (TOF-MS). NH3+ and NH4+ reaction products are detected by applying a 900 ns, -300 V pulse to the extraction plate of the TOF-MS when the desired velocities from the two expansions are inside. Product ions formed outside the TOF-MS are deflected and not detected. The raw number of collected ions is normalized by the reactant densities that are measured separately. The He* beam intensity is monitored by a multichannel plate detector mounted in the beam path, and the density of NH3(J,K = 1,1) is monitored by [2:+1] resonance enhanced multiphoton ionization via the B(v′=5)←X(v′'=0) transition. The overall range in relative velocities covered at each data point, Δv_rel, is ≈30 m/s [4], limited by the pulse duration of about 60 µs of the general valve used for the supersonic expansion of NH3. The conversion of relative velocity to collision energy means that ΔE_coll is the smallest at the lowest energy and determines the minimum accessible collision energy. At the highest collision energies covered here ΔE_coll amounts to several meV.

**Measurement procedure.** The energy dependent cross section σ(E_coll) for the He* + NH3 Penning ionization reaction is obtained by converting the number of acquired ions according to

\[ σ_{v_{rel}}[\text{NH}_3][\text{He}^*] = \frac{\Delta \text{NH}_3^+}{\Delta t} = k(E_{\text{coll}})[\text{NH}_3][\text{He}^*], \quad (3) \]

(and equivalently for NH2+, where k(E_coll) is the measured reaction rate coefficient, and v_rel is the relative velocity. Because the He* and NH3 beams co-propagate in a merged-beam experiment, the relative velocity is simply \( v_{rel} = v(\text{He}^*) - v(\text{NH}_3) \). At the lowest collision energy the average relative velocity is zero, and the distribution of relative velocities is determined by the finite temporal width of the two gas pulses, yielding for the present experiment \( v_{rel} \approx 15 \text{ m/s} \ [4] \).

![FIG. 1. Raw TOF mass spectrum of the He* + NH3 reaction. The solid red line shows the signal from temporally overlapped He* and NH3 beams. The dashed black trace is the background signal arising from the H2O PI by He*, recorded when the NH3 beam is delayed by 3 ms with respect to the He* beam. The inset shows the reactive He* + NH3 signal after background subtraction.](image)

A typical mass spectrum is shown in Fig. 1. The main panel shows the ions collected under conditions where the two gas pulses overlap in time (solid red trace) and where the ammonia pulse is delayed by 3 ms relative to the He* pulse (black dashed line), respectively. The dashed line shows two peaks, at masses 18 and 17, that correspond to (dissociative) Penning ionisation of background water. The solid red trace also contains these ions but in addition, the desired products from the reaction with NH3 are present, namely NH2+ at 16 amu and NH3+ at mass 17. The difference between these two traces, plotted in the inset, shows the background-corrected reactive signal of NH2+ and NH3+ product ions only. A complete excitation function is obtained by recording mass spectra like the one in Fig. 1 for different beam velocities and integrating the ion signals for the respective masses. Such a measurement is performed five times at each collision energy, and the error bars in the data below (Figures 2a and 3) are one standard deviation in the statistical fluctuations for these experiments. Note that cross sections are given in arbitrary units because the determination of absolute reactant densities and beam overlap were not possible in this study.

**Results.** The measured reaction cross section for the two He* + NH3 reactive channels is shown in Fig. 2a. The branching ratio, defined as \( \Gamma = \frac{[\text{NH}_3^+]}{[\text{NH}_2^+] + [\text{NH}_3^+]} \), is displayed in Fig. 2b. The cross section of the He* + NH3 Penning ionization reaction is approximately proportional to \( E_{\text{coll}}^{-1/3} \) at the low energies measured here, as is indicated by the dashed black line in Fig. 2b. A qualitatively similar behavior has been observed in the Ne* + NH3 and Ne* + ND3 reactions [4], and this is indeed expected when the interaction potential is assumed
FIG. 2. Panel a: Experimental cross sections for the production of NH$^+_2$ (upper, red symbols) and NH$^+_3$ (lower, black symbols). The dashed line gives the slope characteristic for a reaction dominated by long-range van der Waals interaction. Panel b: Branching ratio for the production of NH$^+_3$, as defined in the text. The horizontal dashed line at $\Gamma = 0.275$ serves to guide the eye.

Finally, in order to estimate the well depth of the He*-NH$_3$ complex the full ab initio potential energy curve for the collinear geometry of He*-NH$_3$ was studied (see Ref. [4] for geometry description). The supermolecular coupled cluster singles and doubles (CCSD) calculations determined the global minimum to correspond to the He*-lone pair N arrangement, with a bond length of roughly 4.4 bohr and a well depth of 4114 cm$^{-1}$. A local minimum of 60.05 cm$^{-1}$ was found at roughly 9 bohr, corresponding to the He*-H$_3$N arrangement. Those results are consistent with the findings of Ref. [20] for the alkali atom-NH$_3$ complexes. Inversion doubling was neglected in the current calculations. It must be kept in mind, though, that weak coupling between the two potential curves involving the (J,K)=(1,1) rotational level of NH$_3$ might affect the reactivity at certain collision energies.

In QDT it is then noted that the reaction process takes place at distances much shorter than the ones characteristic for the long-range interaction, given by $R_0 = (2\mu C_6/\hbar^2)^{1/4} \approx 46$ bohr. In practice this allows to parametrize the wave function at short distances, either analytically for a pure van der Waals potential, or numerically for a more realistic one, and solve the resulting scattering problem. The key parameters of the model are the short-range reaction probability ($P_{sr}$) and the short-range phase of the wave function (for a detailed description see Refs. 4 and 17).

In the present case, the finite depth of the attractive potential needs to be taken into account. A Lennard-Jones potential $V = -\frac{C_6}{r^6} + \frac{C_1}{r}$ is used for QDT calculations, with the $C_6$ coefficient taken from SAPT and $C_{12}$ adjusted to give the correct well depth. The positions and widths of the resonances can be varied in this simple model by manipulating $P_{sr}$ and the scattering length. However, results obtained this way cannot reproduce the behavior of the data for the lowest collision energies, where the rate constant should approach a constant value, following the Wigner threshold laws [21]. A small potential barrier of $\approx 0.3$ cm$^{-1}$ which slightly suppresses the reaction at the lowest partial waves has to be added to obtain satisfactory agreement (see Figure 3).

Such barriers in general come from avoided crossings or anisotropic term couplings of the partial waves at short range. A reason for such crossing could be the existence of the inversion doubling which has been neglected in the current study [22]. It is possible to model this phenomenon by adding an additional channel to the QDT model, weakly coupled to the entrance. The QDT simulations indeed reproduce a suppressed or enhanced reaction rate, depending on the coupling strength and phase shift in this additional channel, but for a detailed and accurate description of the current problem the model needs further extension.

Figure 3 shows a comparison between the calculated re-
action rate coefficients (lines) and the scaled experimental data (symbols). The dashed blue line gives the raw results from QDT calculation with the potential described in the previous paragraphs. The solid line gives the results convoluted with the experimental resolution. The positions of the observed resonances are well reproduced. The main contributions to the resonances come from the positions of the observed resonances are well reproduced. The solid line gives the results convoluted with the experimental resolution. The positions of the observed resonances are well reproduced. The solid line gives the results convoluted with the experimental resolution. The positions of the observed resonances are well reproduced.

FIG. 3. Comparison of experimental (symbols) and theoretical reaction rate coefficients. The dashed line shows the raw theoretical data, the solid line after convolution with the experimental resolution.

These results represent the first observation of shape resonances in a reaction that involves a polyatomic molecule, and they show that the merged beams technique is a powerful tool to study cold molecular reactions, also of relatively complex polyatomic molecules. Despite this enhanced complexity, resonances were nevertheless observed. The apparent independence of the position of these resonances from the reaction channel appears to indicate that the long range interaction potential in the entrance channel is almost isotropic, which effectively eliminates stereodynamical effects.

Theoretical model basing on the long-range interaction was able to reproduce the experimental results. However, slight discrepancies at low energies show that a more sophisticated treatment, which would include details of the molecular structure and potential surfaces, would give significantly more information about the system and allow for better understanding of the reaction dynamics.

Acknowledgments. We thank Dr. Piotr Żuchowski for useful discussions. Support from the Swiss National Science Foundation (grant number PP0022-119081) and EPFL is acknowledged. K.J. was supported by the Foundation for Polish Science International PhD Projects Pro...
gramme co-financed by the EU European Regional Development Fund. M.H. was supported by the project “Towards Advanced Functional Materials and Novel Devices: Joint UW and WUT International PhD Programme”, operated within the Foundation for Polish Science MPD Programme co-financed by the EU European Regional Development Fund and by the Polish Ministry of Science and Higher Education Grant No. N204 248440.

[1] R. V. Krems, W. C. Stwalley, and B. Friedrich, eds., *Cold Molecules: Theory, Experiment, Applications* (CRC Press, Boca Raton, 2009).
[2] R. D. Levine, *Molecular Reaction Dynamics* (Cambridge University Press, Cambridge, 2008).
[3] J. P. Toennies, W. Welz, and G. Wolf, J. Chem. Phys., 61 (1974).
[4] J. Jankunas, B. Bertsche, K. Jachymski, M. Hapka, and A. Osterwalder, J. Chem. Phys., 140, 244302 (2014).
[5] A. B. Henson, S. Gersten, Y. Shagam, J. Narevicius, and E. Narevicius, Science, 338, 234 (2012).
[6] S. Chefdeville, T. Stoecklin, A. Bergeat, K. Hickson, C. Naulin, and M. Costes, Phys. Rev. Lett., 109, 023201 (2012).
[7] E. Lavert-Ofir, Y. Shagam, A. B. Henson, S. Gersten, J. Klos, P. S. Żuchowski, J. Narevicius, and E. Narevicius, Nat. Chem., 6, 332 (2014).
[8] S. Chefdeville, Y. Kalugina, S. van de Meerakker, C. Naulin, F. Lique, and M. Costes, Science, 341, 1094 (2013).
[9] A. Niehaus, Advances in Chemical Physics, 45, 399 (1981).
[10] B. Bertsche, J. Jankunas, and A. Osterwalder, Chimia, 68, 256 (2014).
[11] J. Jankunas, B. Bertsche, and A. Osterwalder, J. Phys. Chem. A, 118, 3875 (2014).
[12] J. Jankunas, K. Jachymski, M. Hapka, and A. Osterwalder, manuscript in preparation (2014).
[13] M. Ben Arfa, B. Lescop, M. Cherid, B. Brunetti, P. Candori, D. Malfatti, S. Falcinelli, and F. Vecchiocattivi, Chem. Phys. Lett., 308, 71 (1999).
[14] K. Luria, N. Lavié, and U. Even, Rev. Sci. Instrum., 80, 104102 (2009).
[15] U. Even, J. Jortner, D. Noy, N. Lavié, and C. Cossart-Magos, J. Chem. Phys., 112, 8068 (2000).
[16] P. E. Siska, Rev. Mod. Phys., 65, 337 (1993).
[17] K. Jachymski, M. Krych, P. S. Julienne, and Z. Idziaszek, Phys. Rev. Lett., 110, 213202 (2013).
[18] M. Hapka, P. S. Żuchowski, M. M. Szczęśniak, and G. Chałasiński, J. Chem. Phys., 137, 164104 (2012).
[19] C. Schmüttenmaer, R. Cohen, J. Loeser, and R. Saykally, J. Chem. Phys., 95, 9 (1991).
[20] P. S. Żuchowski and J. M. Hutson, Phys. Rev. A, 78, 022701 (2008).
[21] H. Sadeghpour, J. Bohn, M. Cavagnero, B. Esry, I. Fabrikant, J. Macek, and A. Rau, Journal of Physics B: Atomic, Molecular and Optical Physics, 33, R93 (2000).
[22] P. S. Żuchowski and J. M. Hutson, Phys. Rev. A, 79, 062708 (2009).
[23] S. Ospelkaus, K.-K. Ni, D. Wang, M. H. G. de Miranda, B. Neyenhuis, G. Quéméner, P. S. Julienne, J. L. Bohn, D. S. Jin, and J. Ye, Science, 327, 853 (2010).
[24] Z. Idziaszek and P. S. Julienne, Phys. Rev. Lett., 104, 113202 (2010).
[25] M. Mayle, G. Quéméner, B. P. Ruzic, and J. L. Bohn, Phys. Rev. A, 87, 012709 (2013).
[26] G. Quéméner and P. S. Julienne, Chemical Reviews, 112, 4949 (2012).
[27] T. T. Wang, M.-S. Heo, T. M. Ryachov, D. A. Cotta, and W. Ketterle, Phys. Rev. Lett., 110, 173203 (2013).