Production of ArN$^+$ ions in the reactions Ar$^+$ + N$_2$ and N$_2^+$ + Ar

Paolo Tosi, Raffaele Correale, Wenyun Lu, and Davide Bassi

INFM and Dipartimento di Fisica, Università degli Studi di Trento
I-38050 Povo, Trento, Italy


Abstract. We have studied the production of ArN$^+$ starting from the two symmetric charge-state reactants Ar$^+$ + N$_2$ and N$_2^+$ + Ar. For both reactions we measured the total cross sections as a function of the relative energy, in the energy range from 5 to 45 eV. Estimates of the reaction thresholds and symmetry considerations suggest that the reaction Ar$^+$ + N$_2$ produces ArN$^+$ essentially in its first excited state A $^3\Pi$, while the reaction N$_2^+$ + Ar produces ground state ArN$^+$ ions. This fact explains the discrepancies between different estimates of the dissociation energy of ArN$^+$ obtained in previous studies.
Introduction

The charge-transfer reactions:

\[ \text{Ar}^+ + \text{N}_2 \rightarrow \text{N}_2^+ + \text{Ar} \quad (1) \]
\[ \text{N}_2^+ + \text{Ar} \rightarrow \text{Ar}^+ + \text{N}_2 \quad (2) \]

have been extensively investigated for many years.\(^1\)\(^2\) A few years ago, Flesch and Ng\(^3\) measured the integral cross-section of the endoergic reactive channel:

\[ \text{Ar}^+ + \text{N}_2 \rightarrow \text{ArN}^+ + \text{N} \quad (3) \]

Although reaction (3) is a minor process in the argon-nitrogen ion chemistry, its characterization is an essential step towards a more complete understanding of the reaction dynamics of a relatively simple triatomic system as (Ar-N\(_2\))^+. Moreover, the production of ArN\(^+\) is of particular interest since its ground state \(X^3\Sigma^-\) is characterized by a substantial bond between N\(^+\) and Ar in spite of the generally assumed chemical inertness of rare gases.\(^4\)

ArN\(^+\) was first observed in mass spectrometry\(^5\)\(^6\) and its formation was attributed to the reaction of excited N\(_2^+\) ions with Ar. It has also been observed as a minor product in the collision-induced dissociation of the cluster ion ArN\(_2^+\).\(^7\) Spectroscopic information on ArN\(^+\) has been reported by Broström \textit{et al.}\(^8\) More recently ArN\(^+\) has also been observed in the reaction N\(_3^+\) + Ar.\(^9\) An open problem concerns the dissociation energy of ground state ArN\(^+\) ions. \textit{Ab initio} calculations give 2.08 eV\(^4\) and 2.13 eV,\(^10\) whereas experimental estimates are 0.5 eV,\(^3\) 1.22 eV,\(^9\) 2.16 eV,\(^8\) and 2.3 eV.\(^11\)

The measurements of energy thresholds in endoergic ion-neutral reactions may provide information about the dissociation energy of product ions. In the present paper we investigated reaction (3) and the symmetric charge-state reaction:

\[ \text{N}_2^+ + \text{Ar} \rightarrow \text{ArN}^+ + \text{N} \quad (4) \]

Our results suggest that reactions (3) and (4) produce ArN\(^+\) ions in different electronic states. In particular N\(_2^+\) + Ar produces ground state \(X^3\Sigma^-\) ArN\(^+\) ions, while in the reaction of Ar\(^+\) ions with nitrogen molecules, ArN\(^+\) ions are formed mainly in the first excited state \(A^3\Pi\). This finding explains much of the discrepancy between different estimates of the dissociation energy of ArN\(^+\).
Experiment

The results presented here have been obtained with two different experimental setups. Their common key feature is the use of radio-frequency octopole ion guides to guide reactant and product ions. The main difference between the two experiments is that in one setup the guided-ion beam crosses a supersonic molecular beam, whereas in the other machine - hereafter called cell apparatus - the guided-ion beam passes through a room-temperature scattering cell. This second machine is a differentially pumped version of an ion-molecule reaction mass spectrometer previously used in our laboratory.

The cell apparatus provides high sensitivity, but unfortunately the influence of the random motion of the target gas produces a significant dispersion of the collision energy. The effective cross section, measured at the nominal relative energy \( E_0 \), results from the convolution of the reaction cross section \( \sigma(E) \), where \( E \) is the relative energy, with the energy distribution \( f(E,E_0) \) of reactants:

\[
\sigma_{\text{eff}}(E_0) = \int_0^\infty \frac{E}{E_0} f(E,E_0) \sigma(E) dE
\]

If \( T \) is the temperature of the scattering cell, and assuming that \( E_0 >> k_B T \), where \( k_B \) is the Boltzmann's constant, the energy distribution function \( f(E,E_0) \) is centered around \( E_0 \), with a FWHM given by:

\[
\Delta E_0 \approx \sqrt{\frac{11.1 m_I}{m_I + m_N} k_B T E_{\text{cm}}}
\]

where \( m_I \) and \( m_N \) are the ion and the neutral mass, respectively. For reaction (3), measured by means of the room-temperature cell machine, \( \Delta E_0 \) is about 1 eV at the relative energy of 6 eV.

The alternative approach is based on the use of the crossed-beam apparatus. The molecular beam is produced by the supersonic expansion of neutral molecules through a nozzle which can be cooled to 150 K. A collimator in front of the octopole, where the two beams cross at 90°, reduces the angular divergence of the supersonic beam to about 1°. The crossed-beam apparatus is much less sensitive with respect to the cell apparatus, and measurements may be very time consuming. However it provides a much better energy resolution.
The combined use of the two machines enable us to set up a very effective measurement strategy. Ion-molecule reactions are first investigated using the high-sensitivity cell apparatus. The crossed-beam machine is then used to repeat the measurements only at a limited number of collision energies, studying in more details the regions where a better resolution is required.

**Results and discussion**

\[ \text{Ar}^+ + \text{N}_2 \rightarrow \text{ArN}^+ + \text{N} \]

The comparison between results obtained in the present work and data obtained in previous experiments\(^3\) is shown in Fig. 1. Our results are scaled to their absolute cross sections near the maximum. The energy dependences of the cross sections measured in the two different laboratories are in very good agreement.

![Figure 1. Energy dependence of the total cross-section for reaction (3). Results of our cell experiment (line) are compared with those of Flesch and Ng.\(^3\)](image)

In Fig. 2 we compare the results of the cell experiment (full line) with those ones obtained in the crossed-beams experiment (points). A deviation is observed at collision energies below about 10 eV. It is clearly due to the different energy...
resolution of the two experiments. Crossed-beam results show - as expected - a sharper reaction onset, but a poorer signal-to-noise ratio.

Figure 2. Energy dependence of the total cross-section for reaction (3) measured by means of the cell machine (full line) and the crossed-beam machine (points). The energy dependence for the symmetric charge-state reaction (4) is shown by means of a dashed line. Cross sections are reported in arbitrary units, normalized on the maximum. The absolute value of the cross-section for reaction (4) is about 0.05 Å² at the collision energy of 18 eV.

Of particular interest here is the determination of the reaction threshold $E_{TH}$, since it is related to the dissociation energy, $D_0$, of the ground state product ion $\text{ArN}^+$. The relationship between these two quantities is:

$$E_{TH} = \Delta H(\text{ArN}^+) + \Delta H(\text{N}) - \Delta H(\text{Ar}^+)$$

where $\Delta H$ is the enthalpy of formation and:

$$\Delta H(\text{ArN}^+) = \Delta H(\text{N}^+) - D_0(\text{N}^+ - \text{Ar})$$

Flesch and Ng\textsuperscript{3} measured the threshold energy for $\text{ArN}^+$ to be $E_{TH} = 8.24 \pm 0.21$ eV and from this value they estimated the dissociation energy of $\text{ArN}^+$ to be approximately 0.5 eV. Unfortunately these values appear to be irreconcilable either with theoretical calculations of the dissociation energy (2.08 eV\textsuperscript{4} and 2.13 eV\textsuperscript{10}) and with its spectroscopic estimate of 2.16 eV, obtained by the analysis of the photoabsorption spectra in the visible wavelength region.\textsuperscript{8}
The estimation of energy thresholds in endoergic reactions may be a complex matter. Typically one has to choose a functional form, $\sigma(E)$, to reproduce the energy dependence of the cross section. This function contains at least one free parameter, the value of the threshold energy, $E_{TH}$. After the appropriate convolutions over the energy distribution of the reactants, the calculated cross sections are compared with the experimental data and $E_{TH}$ is obtained by an iterative fitting procedure. Unfortunately results of these calculations depend critically on both the experimental signal to noise ratio (SNR), and the functional form assumed for the cross section. Concerning the first point, a decrease in the SNR typically may produce a shift of the observed reaction onset towards higher energies. On the other hand, the choice of $\sigma(E)$, and in particular the number of free parameters that are included in the function, can strongly affect the results of the whole procedure.\textsuperscript{17,18} A commonly used approach assumes that the energy dependence in the threshold region can be analyzed with a model cross section of the form:

$$
\sigma(E) = \sigma_0 (E - E_{TH})^n / E
$$

where the energy threshold $E_{TH}$, $\sigma_0$ and $n$ are adjustable parameters.

By following this recipe, the analysis of our crossed beam experiment yields a threshold of $8.9 \pm 0.2$ eV, whereas from the data obtained in the cell apparatus we obtain a threshold of $8.2 \pm 0.5$ eV. The discrepancy between these two values can be understood taking into account the different SNR in the two experiments, as discussed in the previous section.

Despite the fact that it is not possible to extract a precise value for the reaction threshold, our experiments confirm the results of Flesch and Ng,\textsuperscript{3} and show that the onset for reaction (3) occurs at a threshold between 8.2 and 8.9 eV. On the other hand, if the spectroscopic value $D_0 = 2.16$ eV\textsuperscript{8} is used together with the well known thermochemical values $\Delta H\left(N^+\right) = 19.413$ eV, $\Delta H\left(\text{Ar}^+\right) = 15.760$ eV, and $\Delta H(N) = 4.879$ eV, one calculates $\Delta H(\text{ArN}^+) = 17.25$ eV and $E_{TH} = 6.37$ eV. In other words if the ArN$^+$ ions formed in reaction (3) have a dissociation energy of 2.16 eV, then the reaction threshold should be at 6.37 eV and not above 8 eV as experimentally determined. One possibility is that a barrier is responsible for the difference in threshold energies. However, a second possibility is that product ions formed in reaction (3) are in their first excited state, whose energy has been calculated about 2
eV above the ground state. Indeed the estimate of about 0.5 eV\textsuperscript{3} for the dissociation energy of ArN\textsuperscript{+} is close to the 0.2 eV calculated for the first excited state.\textsuperscript{8} Further hints come from the state correlation diagram discussed later on.

\[
\text{N}_2^+ + \text{Ar} \rightarrow \text{ArN}^+ + \text{N}
\]

In Fig. 2 we compare the energy dependencies of the cross sections of reactions (3) and (4). Cross sections are reported in arbitrary units, normalized at their maxima. The absolute value of the cross section for reaction (4) is about 0.05 Å\textsuperscript{2} at a collision energy of 18 eV.

Though the cross sections of reactions (3) and (4) show a quite similar energy dependence, some differences appear to be significant. The first difference concerns the reaction onset, that for reaction (4) appears at a lower relative energy. The analysis of the data yields an energy threshold of 5.7 ± 0.5 eV. Thermochemistry calculations for the production of ground state ArN\textsuperscript{+} ion in reaction (4) indicate an energy threshold of 6.6 eV. The discrepancy of about 1 eV between theoretical and experimental numbers appears to be outside the experimental errors and at the present it is not fully understood. It might partially due to the presence in the primary ion beam of excited N\textsubscript{2}\textsuperscript{+} ions, in spite of the careful selection of the ionization conditions (low electron energy, high gas pressure). Under any circumstances, experimental results clearly suggest that reaction (4) produces ground state ArN\textsuperscript{+} ions.

The second difference between reaction (3) and (4) concerns the position of the maximum in the plot of the cross section versus the collision energy. In particular, the maximum for reaction (4) occurs at about 18 eV, while that for reaction (3) is located at about 15 eV (see Fig. 2). The position of the maximum has often been related to the dissociation energy of the product ion, the declining of the cross section at higher energies being attributed to the increasing dissociation of product ions.\textsuperscript{19} The late declining of reaction (4) compared with reaction (3) thus suggests an higher stability for ArN\textsuperscript{+} ions formed by process (4) compared with those formed by reaction (3). Once more this is consistent with previous hints that the two reactions form ArN\textsuperscript{+} products in different electronic states.
State correlation diagram

Many experimental findings can be understood on the base of a simple diabatic state correlation diagram, for which we need the energies of the reactant and product states. The first low-lying states are shown in Fig. 3, along with diabatic correlations between reactants and products.

![Diabatic correlation diagram](image)

Figure 3. Diabatic correlation diagram for reactions (3) and (4). Full lines corresponds to the two spin orbit state of Ar⁺ (reaction (3)), while dashed lines corresponds to the first three low-lying states of $N_2^+$ (reaction (4)). See text for details.

From the calculations of Broström et al.\textsuperscript{8} we know that both of the two lowest bound states of ArN\textsuperscript{+} dissociate to the $N^+ (3P) + Ar (1S)$ limit. Therefore one can correlate diabatically these states to the corresponding lowest states of $N_2^+ + Ar$ having the same symmetry, that in the two-body asymptotic limit are of $\Sigma$ and $\Pi$ type. This is shown in Fig. 3 by the lines connecting $N_2^+(X 2\Sigma) + Ar(1S)$ with ArN\textsuperscript{+}(X 3\Sigma) + N(4S) and $N_2^+(A 2\Pi) + Ar(1S)$ with ArN\textsuperscript{+}(A 3\Pi) + N(4S), respectively. Accordingly, these state correlations corroborate the experimental suggestion that reaction (4) produces ground state ArN\textsuperscript{+} ions.

Concerning reaction (3), the diagram shows that Ar\textsuperscript{+}(2P) + $N_2 (1\Sigma)$ cannot correlate diabatically with the X and A states of ArN\textsuperscript{+}, since these dissociate to $N^+ +$
Ar. Instead the surfaces evolving from the Ar$^+$ + N$_2$ reactants (full lines in Fig. 3) correlate diabatically with high excited states of ArN$^+$ dissociating to the Ar$^+$ + N limit. Consequently, the reaction of Ar$^+$ ions with N$_2$ to produce ArN$^+$ in the first two low-lying states proceeds via charge transfer to a N$_2^+$ + Ar surface.

The scattering between Ar$^+$(2P$_{3/2}$) and N$_2$(X 1Σ) occurs on two potential energy surfaces which, at short range, have Π character for C$_{nv}$ symmetry. The two Π surfaces evolving from Ar$^+$(2P$_{3/2}$) to repulsive states of ArN$^+$ cross the diabatic surface evolving from N$_2^+$(A 2Π) + Ar(1S) to ArN$^+$(A 3Π) + N(4S). These surface crossings are avoided such that the reaction Ar$^+$(2P$_{3/2}$) + N$_2$ leads adiabatically to the first excited ArN$^+$ (A 3Π) state.

As far as Ar$^+$(2P$_{1/2}$) + N$_2$ is concerned, this surface has Σ character and therefore can be coupled with the vibronic states of the charge-transfer complex N$_2^+$(X 2Σ) + Ar(1S). For example, the avoided crossing between the Ar$^+$(2P$_{1/2}$) + N$_2$ and the N$_2^+$(X 2Σ, v = 2) + Ar(1S) surfaces leads to an adiabatic correlation of Ar$^+$(2P$_{1/2}$) + N$_2$ with the ground state of ArN$^+$.

It should however be remembered that the above symmetry considerations are only a first approximation, since pure Σ and Π characters are acquired only at short range. At large and intermediate distances, the spin-orbit interaction mixes the Σ and Π characters, resulting in possible couplings (neglected in the present qualitative model) between surfaces of different symmetry.

In conclusion, it appears that while reaction (4) produces essentially ground state products, reaction (3) may produce ArN$^+$ either in its ground state and in its first excited state. It should however be noted that the comparison between avoided crossings of Π and Σ symmetry shows that Σ crossings are passed with a higher radial velocity, given a certain relative energy. Thus the behavior of the system at the Σ crossings should be more diabatic and the reaction less effective. This consideration, in addition to the different number of states of Π (2 states) and Σ (1 state) symmetry, suggests that Ar$^+$(2P$_{1/2}$) should be less reactive than Ar$^+$(2P$_{3/2}$) and therefore that reaction (3) produces essentially ArN$^+$(A 3Π), in agreement with measurements of the reaction endothermicity.
Conclusions

In the present paper we have studied the production of ArN⁺ starting from the two symmetric charge-state reactants Ar⁺ + N₂ and N₂⁺ + Ar. For both reactions we have provided total cross sections as a function of the relative energy, extending the work described in Ref. 3. Estimates of the reaction thresholds and symmetry considerations suggest that the reaction Ar⁺ + N₂ produces ArN⁺ essentially in its first excited state A³Π, while the reaction N₂⁺ + Ar should produce ground state ArN⁺ ions. This fact explains the discrepancies between different estimates of the dissociation energy of ArN⁺ obtained in previous studies.

Further experiments devoted to the study of the internal energy distribution of the product ions would be of great help for confirming the present results and for providing more insight into the reaction dynamics of the (Ar-N₂)⁺ system. In addition, experiments with state selected Ar⁺ ions could address the problem of the different reactivity of the two spin-orbit states, as already done for the charge-exchange channel.²⁰

We acknowledge stimulating discussions with D. Cappelletti, S. Falcinelli, F. Pirani, and R. Tarroni.

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