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Non-dissociative collisions at 0.3-3 keV

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To cite this version:
J. Fayeton, A. Pernot, P. Fournier, M. Barat. Collisions of N+2 ions on noble gas atoms II. Non-dissociative collisions at 0.3-3 keV. Journal de Physique, 1971, 32 (10), pp.743-750. <10.1051/jphys:019710032010074300>. <jpa-00207131>

HAL Id: jpa-00207131
https://hal.archives-ouvertes.fr/jpa-00207131
Submitted on 1 Jan 1971

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COLLISIONS OF N$_2^+$ IONS ON NOBLE GAS ATOMS
II. NON-DISSOCIATIVE COLLISIONS AT 0.3-3 keV
J. FAYETON (*), A. PERNOT (*), P. FOURNIER (**), and M. BARAT (*)
(Reçu le 11 mars 1971)

Résumé. — Nous avons étudié la diffusion d'ions moléculaires N$_2^+$ par différentes cibles de gaz rares (He, Ar, Xe) dans la gamme d'énergie 0,3-3 keV et pour des angles de diffusion de 0,8° à 7°.
Une analyse en énergie des ions diffusés sans dissociation met en évidence plusieurs processus collisionnels :
— Diffusion élastique et excitation vibrationnelle-rotationnelle de l'ion incident.
— Excitation électronique du projectile et de la cible.
Nos résultats relatifs au premier processus sont comparés au modèle binaire, proposé par V. I. Gerasimenko. Les mécanismes d'excitations sont interprétés selon un même schéma. Simultanément à l'excitation vibrationnelle il peut se produire une excitation électronique de la cible ; pour interpréter ce phénomène nous avons été amenés à considérer le complexe quasi moléculaire formé par la molécule et l'atome cible au moment de la collision. Les croisements de surfaces de potentiel du complexe sont déterminants pour les différentes voies de sortie.

Abstract. — Scattering without dissociation of N$_2^+$ molecular ions by noble gas atom targets (Xe, Ar, He) is investigated. In the laboratory coordinate system, the collision energy ranges from 0.3 to 3 keV and the scattering angles from 0.8° to 7°. An energy loss analysis of the scattered N$_2^+$ ions shows several competitive processes :
— Elastic scattering and vibrational excitation.
— Electronic excitation of projectile and target.

For the first of these processes our results are compared with the binary model proposed by V. I. Gerasimenko and J. D. Oksjuk, and T. A. Green. The different excitation processes are interpreted in the same way ; particularly the simultaneous electronic and vibrational excitations are investigated. During the collision molecule and target are considered as a quasi-molecule complex decaying into several channels via potential surface crossing.

I. Introduction. — Up to now, most of the work concerning collisions between molecular ions and atoms has been restricted to dissociative processes at relatively large incident energies (above 2 keV) [1]. Particularly it has been shown that dissociation occurs mainly through two kinds of excitation :
(i) Electronic excitation via a repulsive or a pre-dissociative state.
(ii) Adiabatic vibrational and/or rotational excitation towards the continuum of the initial state.

The second mechanism has been tentatively explained through a two-step model proposed by V. I. Gerasimenko and J. J. Oksjuk [2] and developed by T. A. Green [3]. In this simple model, called the « binary model », the dissociation is considered to take place via two independent steps :
— The first one is a binary collision involving the target atom and only atom of the molecule. In this step, the second atom behaves like a « spectator ».
— Then the molecular ion is an isolated system so that the energy received by the active atom is partially transformed into internal energy of the molecule (such as vibrational excitation).

Provided the incident energy is large enough and the targets are light, a good agreement is achieved with experimental cross section measurements.

In such a model, the second step is independent from the way the energy transfer $\Delta E$ happened between the colliding particles, i. e., for a given $\Delta E$, the probability of excitation towards a final state (vibrational continuum as well as bound state) can be calculated independently from the collision problem. This remark can serve as an introduction to experiments involving molecular ion-atom collisions without dissociation in which this model can be checked more directly.

Moreover, that kind of experiment permits the study of target excitation mechanisms which are not easily detectable in collision-induced dissociation experiments.

This paper is a report of differential measurements of N$_2^+$ ions scattered without dissociation by noble gas targets (He, Ar, Xe) the dissociative processes being studied in the accompanying paper [4].
By a scattered ion energy analysis, a detailed study of the energy transfer involved in the different colliding systems is carried out, in terms of the scattering angle and the incident energy. In addition differential cross section measurements are given for some of these processes. Then the results are discussed in the frame of the binary model.

The $N^+_2$ is chosen as projectile because its potential well is deep enough to allow an easy energy loss analysis related to the vibrational excitation process, in spite of the relatively large energy spread of the ion beam. The laboratory energy ranges from 0.3 to 3 keV and is low enough to prevent dissociative processes from being important.

2. Apparatus and experimental procedure. — Only a brief review of the experimental set-up will be given here; a more detailed description can be found elsewhere [5].

$N^+_2$ molecular ions (*) are produced in a low pressure, low anode voltage, hot cathode positive ion glow discharge. The ions are then extracted, focussed, collimated into a beam and enter the collision chamber. The collision space is located at the crossing of the incident ion beam and of a target atom thermal beam. The energy of the scattered molecular ions is analyzed by a 127° cylindrical electrostatic sector, with a typical energy resolution $\Delta E/E = 2 \times 10^{-3}$.

The voltage between the plates of the electrostatic analyser is set on the incident beam, and the energy analysis of the scattered particles is achieved by giving to the scattered molecular ions a known small amount of energy so that they pass through the electrostatic sectors. Afterwards the scattered ions are individually counted with a tubular electron multiplier.

The resulting experimental data appear on intensity curves versus energy loss for a given scattering angle.

Due to the lack of incident ion mass analysis, the discharge voltage is kept low enough ($V \simeq 25$ V) to insure that the $N^+$ contribution is negligible (this was checked experimentally).

The energy spread (typically 0.5 eV) of the incident beam is mainly limited by the ion source. Moreover the energy resolution of the scattered ion data is limited by the energy spread due to the finite angular resolution $\delta \theta^2$, their relation being

$$\delta(\Delta E) = 2 \frac{M_{ab}}{M_e} E_o \delta \theta,$$

where $\delta \theta = 2 \times 10^{-3}$ rad, and $M_{ab}$, $M_e$ are respectively the molecular ion and the target mass.

In order to improve the energy resolution the scattered ions are decelerated down to 0.5 keV before analysis.

(*) In our experiment the $N^+_2$ incident beam is mainly composed of 90 % of $X^2 \Sigma^+_g$ ground state ($v = 0$, $v = 1$) ions and of 10 % of first electronic excited state $A^2 \Pi_u$ ions [6].

In the experimental procedure, the target pressure is kept low enough to insure that only simple collisions occur.

3. Results. — Some energy loss spectra are displayed in figures 1, 2, 3 for different targets, angles and energies.

![Figure 1](image1.png)  
**FIG. 1.** — Energy loss analysis of $N^+_2$ ions scattered by xenon atoms: peak « A » « pseudo-elastic » process ; peak « B » $N^+_2$ electronic excitation ; peak « C » Target excitation.

![Figure 2](image2.png)  
**FIG. 2.** — Energy loss analysis of $N^+_2$ ions scattered by argon atoms : peak « A » « pseudo-elastic » process ; peak « B » $N^+_2$ electronic excitation ; peak « C » Target excitation.
FIG. 3. — Energy loss analysis of N$_2^+$ ions scattered by helium atoms: peak « A » « pseudo-elastic » process, peak « B » Electronic excitation of N$^+$; peak « C » Simultaneous electronic excitations of N$_2^+$ and He.

Generally three processes can be observed:

(i) Elastic and vibrational excitation (peak A).
This process will be called « pseudo-elastic » scattering. It can be noticed that the energy resolution is not sufficient to resolve the different vibrational levels.

(ii) Electronic excitation of N$^+$ (peak B).

(iii) Excitation of the target (peak C).

3.1 ELASTIC AND VIBRATIONAL EXCITATION. — Before giving results it is necessary to recall the theoretical values of the kinetic energy loss undergone by an incident particle scattered at a $\theta$ angle.

The following notations will be used throughout this paper:

$E_0$ : initial translational energy of the N$_2^+$ ions in the laboratory system.

$\Delta E$ : energy loss of the scattered N$_2^+$ ion.

$M_{ab}$ : mass of the molecular N$_2^+$ ion.

$M_a$ : mass of the nitrogen atom.

$M_e$ : mass of the target atom.

$\theta$ : Laboratory frame scattering angle.

$\chi$ : Scattering angle in the $M_a - M_e$ Center of mass coordinates.

According to the binary model, in the first step we have to consider the elastic scattering of only one atom of the molecular ion by the target atom: the kinetic energy loss undergone by this atom $a$ is given:

$$\Delta E_1 = 2 \frac{M_a M_e}{(M_a + M_e)^2} E_0 (1 - \cos \chi)$$

in the second step $\Delta E_1$ is partially turned into internal energy of the ab molecular ion (vibrational or rotational energy)

$$\Delta E_{int} = \left( \frac{M_a M_e}{(M_{ab})^2} \right) \cdot \Delta E_1 = \left( \frac{M_a M_e}{M_{ab}(M_a + M_e)} \right)^2 2 E_0 (1 - \cos \chi)$$

the center of mass scattering angle $\chi$ is easily given in terms of the laboratory scattering angle $\theta$ of the molecule

$$\tan \theta = \frac{\sin \chi}{(M_{ab}) (M_a + M_e) - 1} + \cos \chi.$$ 

Then the energy loss $\Delta E_0$ of the scattered ions is the sum of the internal energy $\Delta E_{int}$ and of the kinetic energy $\Delta E_{k1}$ given to the target particle (elastic energy)

$$\Delta E_{el} = 2 E_0 \left( \frac{M_{ab} M_e}{(M_e + M_{ab})^2} \right) (1 - \cos \chi)$$

$$\Delta E_0 = \Delta E_{int} + \Delta E_{el}.$$ 

Since these experiments are generally made with small scattering angles we can use an approximate formula directly giving the experimental energy loss in terms of the laboratory scattering angle $\theta$:

$$\Delta E_0 = \left( \frac{M_{ab} + M_e}{M_e} \right) E_0 \theta^2$$

on the other hand a different model (« elastic model ») considers the molecule as formed by two atoms at a constant internuclear distance so that, in this rigid model, the molecule can be considered as an atom and the energy loss is then given by

$$\Delta E_{el} = \frac{M_{ab}}{M_e} E_0 \theta^2 \quad \text{(for small values of } \chi).$$

In order to directly compare the energy data independently from the incident energy, the energy losses are given versus $E_0 \theta^2$; as long as the C. M. scattering angle $\chi$ is small enough, the energy loss varies linearly with $E_0 \theta^2$ (this is not valid for the N$_2^+$-He data)

N$_2^+$-Xe.

Energy loss diagrams of N$_2^+$ scattered by Xe atoms are shown in figure 4 for different incident energies (0.5, 1, 2 and 3 keV). The theoretical values of $\Delta E_{el}$ and $\Delta E_0$ are given on this diagram. It is noteworthy that $\Delta E_{el}$ is dependent on the incident energy $E_0$ and is only a function of the product $E_0 \theta^2$.

For small scattering angles ($\theta \leq 2^\circ$) our data closely agree with the binary model. On the other hand a break on the $\Delta E_{el}$ curve can be noticed near $E_0 \theta^2 = 4 \times 10^4$ eV (d)$^2$,

the $\Delta E_{el}$ curve becoming parallel to the elastic model energy loss $\Delta E_{el}$: This behaviour is easily explained if the maximum vibrational energy transfer is limited by the potential well depth; a larger energy transfer induces a dissociative process, since the energy difference $\Delta E_0 - \Delta E_{el}$ between the two models corresponds to the transferred vibrational energy.
FIG. 4. — Energy losses of N$^+$ scattered by xenon : $\Delta E_{\text{p-el}}$ « pseudo-elastic » energy loss ; $\Delta E_2$ N$_2^+$ electronic excitation loss ; $\Delta E_3$ Xenon excitation loss ; Curve 1 « Binary » energy loss $\Delta E_b$ ; Curve 2 Elastic energy loss $\Delta E_e$ ; Curve 3 Asymptotic curve of the binary energy loss ; impact energy (laboratory coordinates) : + (.5 keV), 0 (1 keV), A (2 keV) D (3 keV).

The asymptotic curve 3, drawn in a direction parallel to the curve 1 at a distance equal to the potential well, shows this maximum energy transfer. The experimental data are in good agreement with this limit $N_2^+\text{-Ar}$.

Energy loss diagram of $N_2^+$ scattered by Ar atom is shown in figure 5. For a given incident energy the experimental points are disposed along a straight line showing a linear dependence of $\Delta E_{\text{p-el}}$ versus $\theta^2$. When $E_0$ varies, only the slope of the experimental curve changes, inferring that the real process becomes close to the binary model when the energy increases. As in the previous case, above

$$E_0 \theta^2 = 3 \times 5 \times 10^4 \text{ eV (d)}^2,$$

the experimental curves follow the asymptotical curve 3. Nevertheless, for the largest values of $E_0 \theta^2$, the experimental data show that the maximum vibrational excitation transfer becomes smaller than the limit value $N_2^+\text{-He}$.

Since the incident particle has a much larger mass than the target, the energy spread caused by the finite angular resolution is relatively important and of the same order of magnitude as the involved energy losses. In addition, the previously used approximate formulas of $\Delta E_b$ and $\Delta E_{\text{el}}$ are no longer valid.

Consequently the energy loss given by the two models are not a linear function of $E_0 \theta^2$ (see Fig. 6). For all incident energies, experimental results are in quite a good agreement with the binary scattering model. However, for scattering angles below 3°, the experimental data are at about 3 eV above the theoretical curves this anomaly can be thus explained : if during the scattering each atom of the molecule receives symmetrically the same momentum transfer, the molecule is vibrationally excited without deviation of its center of mass.

3.2 ELECTRONIC EXCITATION OF $N_2^+$. — The scattering of the molecular ion $N_2^+$ by an atomic target can give rise to a second process : the electronic excitation of the $N_2^+$ projectile :

$$N_2^+ \left( X^2 \Sigma_u^+ \upsilon = 0 \right) + C \rightarrow \left( N_2^+ \right)^* + C + Q$$

$$Q \approx 8.5 \text{ eV}.$$

Indeed the 8.5 eV peak B cannot be assigned to a target excitation level, besides similar energy loss peaks are found whatever the target is (Fig. 1, 2, 3). The assignment of the involved electronic level will be discussed below.

As in a previous case the energy loss measurements $\Delta E_2$ are investigated in the frame of the different models.

$\Delta E_2$ data ($N_2^+$ electronic excitation) figures 4, 5, 6. It can be noticed that these curves are parallel to the elastic model $\Delta E_{\text{el}}$ curves. The constant difference between them is assigned to the electronic excitation of the projectile. This difference $\Delta E$ is about 8.5 eV. The parallelism between the projectile excitation curves and the elastic model curves shows that no vibrational excitation occurs in this excitation mechanism.
The potential energy curves of N⁺ (Fig. 7) are given by F. R. Gilmore [7]. The experimental excitation energy has been compared with the energy gap between the initial ground state of N⁺ (X²Σ⁺, v = 0) and the available excited stages, taking the Franck-Condon principle into account.

Any excited electronic state is compatible with the 8.5 eV experimental excitation value. Nevertheless two excited states (C²Σ⁺ and ⁴Πg) have an energy close enough to the experimental energy loss to be considered as probably excited.

In order to explain the apparent disagreement between theoretical and experimental energies we propose that this excitation take place through and « oblique » transition.

Actually, during the collision, the N⁺ molecular energy curves are disturbed by the target atom and the real transition occurs between the « modified » energy curves (see discussion).
4. Electronic excitation of the target. — $N_2^+$-Xe.

As shown in figure 1 the peak C is assigned to a single excitation of Xenon:

$$N_2^+ + \text{Xe} \rightarrow N_2^++\text{Xe} \quad (5\ p^5,\ nl)$$

The width of this excitation peak cannot be explained by the energy spread only. Several states are probably excited but the resolution is not good enough to resolve each excited state.

The energy loss $\Delta E_3 = f(E_0\theta^2)$ curves are shown on figure 4. Contrary to the previous projectile excitation case, the $\Delta E_3$ curve is parallel to the « pseudo elastic » one, showing a simultaneous vibrational excitation of $N_1$.

$N_2^+$-Ar. — Similar results are found for the $N_2^+$-Ar collision in which Ar $(3\ p^5\ nl)$ excitations take place. Nevertheless, the first excited levels are not so close to one another, therefore the $4\ s$ excited level is separated from the remaining states (Fig. 2).

$N_2^+$-He. — As explained before, the energy resolution is lost, however the results are similar to those of the other targets (Fig. 6).

5. Cross-sections. — The differential cross sections ($\rho = f(E_0\theta)$) for each process are shown on figure 8 for several incident energies and colliding systems. The differential cross sections are given only in relative value.

The projectile excitation differential cross sections ($\rho_2$) present a maximum close to:

- $E_0\theta = 1\ 500\ eV\cdot d^0$ for He
- $E_0\theta = 2\ 000\ eV\cdot d^0$ for Ar
- $E_0\theta = 1\ 000\ eV\cdot d^0$ for Xe

This maximum occurs with a given target for the same $E_0\theta$ value, whatever the incident energy. Furthermore $\rho_2$ decreases with the incident energy.

This behaviour should be in agreement with an excitation process, taking place via a pseudo crossing of $N_2^+$-target potential energy surface (see discussion).

The differential cross section for every target excitation behaves in the same way as observed in the previous case. On the other hand the relative cross section increase with the energy, showing that the involved crossing is no longer adiabatic. Nevertheless we can notice that the crossing involved in the target excitation occurs at a lower value of the internuclear distance $R$ than the $N_2^+$ excitation crossing.

6. Discussion. — We made these experiments first to check the validity of the binary model: whatever the target, the agreement between theory and experiment is good for the higher energies ($\geq 2\ \text{keV}$) used in this work. It appears that, effectively, the second atom of the molecular ion acts as a « spectator » during the collision. On the other hand, for the lower impact energies, the behaviour is different according to the target. With helium, the good agreement is preserved but with heavier targets, no definitive conclusion can be drawn. Argon and Xenon showing very different results. The process seems to be close the binary model with Xe as the target but with Ar the experimental results lead to an elastic process interpretation. This last result was expected, because at low energy and for small angles, the collisions are more gentle and the impact parameter is larger; the distance between the target and each atom of the molecule becomes of the same order of magnitude. Therefore the difference between the interactions of the target with each atom is weaker than the binding energy of the molecule. But for $N_2^+$-Xe, the results are more surprising and no explanation can be proposed at the present time.

Let us now consider the excitation of the target. From the experimental results this excitation occurs in addition to the vibrational excitation of the molecule.

These two processes have a common feature which is well explained by the two steps binary model. Only the first step is different from the « pseudo elastic » process: if the distance of the closest approach is too large to reach the pseudo crossing line (Fig. 9) (a generalisation in 3 dimensions of the well known crossing point), no excitation takes place and only vibrational excitation occurs. For more violent collisions, when the crossing line is reached, the transition from the $(N_2 - \text{target})^+$ quasi-molecular ground state to an excited state occurs. According to the outgoing channel of the $(N_2 - \text{target})^+$ quasi-molecule, only two new kinds of process are expected in this energy range.

(i) $N_2^+ + \text{Target} \rightarrow N_2^+ + (\text{Target})^*$
(ii) $N_2^+ + \text{Target} \rightarrow (N_2^+)^* + \text{Target}$

The first one decays into an excited state of the target, $N_2^+$ remaining in the electronic ground state. The
Fig. 8. — Differential cross sections for «pseudo-elastic» ($p_1$) projectile excitation ($p_2$) and target excitation ($p_3$). Reduced cross sections $\rho = \Sigma \theta \sin \theta$ are given as functions of the product $\tau = E_0 \theta$ [9]. Impact energy — 5 keV ... 1 keV — — — — 2 keV — — — — 3 keV; 8a: Xenon target; 8b: Argon target; 8c: Helium target.
second step of the process is the same as the one in the pseudo elastic case. Therefore, the N$_2^+$ exit channel being the same, a similar vibrational excitation is expected, as is shown by the experiment.

The second one induces an electronic excitation of N$_2^+$. In this case the N$_2^+$ state exit channel is different from the input one. Therefore, in the second step, we should expect a simultaneous vibrational excitation of (N$_2^+$)*. Two excited channels being available, if we first consider the $^4\Pi_u$ state as the exit channel, only very few vibrational levels are present up to the 8.5 eV dissociation limit, which is in good agreement with the very small amount of vibrational excitation experimentally observed in the present case.

Let us now consider the C$^2\Sigma_u^+$ state of N$_2^+$ excited as being involved in the channel, this state being crossed by the $^4\Pi_u$ state in an adiabatic collision. Then as already proposed by Rosenthal [8] for atomic ion-atom collision, a two crossing process can be considered:

- At the first crossing a transition occurs leading to the C$^2\Sigma_u^+$ state;
- At larger internuclear distances the second C$^2\Sigma_u^+$ -- $^4\Pi_u$ crossing is reached and therefore the $^4\Pi_u$ becomes a possible exit channel.

It is remarkable that, by accident the excitation energy involved is about the same as that involved in the previous C$^2\Pi^+_u$ case, and no definite conclusion can be drawn.

Acknowledgements. — The authors wish to thank Pr. J. Durup and Dr. J. Baudon for valuable discussions and helpful suggestions throughout the course of this work.

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