Collisions of N+2 ions on noble gas atoms I - Collision induced dissociation of N+2
P. Fournier, A. Pernot, J. Durup

To cite this version:
P. Fournier, A. Pernot, J. Durup. Collisions of N+2 ions on noble gas atoms I - Collision induced dissociation of N+2. Journal de Physique, 1971, 32 (7), pp.533-541. <10.1051/jphys:01971003207053300>. <jpa-00207107>

HAL Id: jpa-00207107
https://hal.archives-ouvertes.fr/jpa-00207107
Submitted on 1 Jan 1971

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
COLLISIONS OF N$_2^+$ IONS ON NOBLE GAS ATOMS

I. — COLLISION INDUCED DISSOCIATION OF N$_2^+$

P. FOURNIER (*), A. PERNOT (**) and J. DURUP (*)

(Reçu le 15 février 1971)

Résumé. — La dissociation d’ions N$_2^+$ de 0,35 à 4,4 keV par collision avec des cibles de He ou Xe a été étudiée à l’aide de deux appareils différents. La mesure des distributions de vitesses des fragments N$^+$, à énergie variable des électrons utilisés pour produire les ions parents N$_2^+$, a permis de mettre en évidence sept processus différents ; pour la plupart d’entre ceux-ci les énergies internes de l’ion et de la cible à l’état initial et à l’état final ont été déterminées. Des interprétations des transitions mises en jeu sont proposées.

Abstract. — The dissociation of 0.35 to 4.4 keV N$_2^+$ ions following collision on He or Xe targets was studied with two different apparatus. From the measurement of N$^+$ fragment velocity distributions at varying energies of the electrons used to produce the parent N$_2^+$ ions, seven different processes were shown to occur ; for most of them the internal energies of the ion and the target in their initial and final states were determined. Tentative interpretations of the involved transitions are given.

Introduction. — The velocity spectra of N$^+$ ions arising from collisions of N$_2^+$ ions on various targets have been studied by several workers [1 - 5]. From the experiments performed in the $10^4$ eV energy range one may distinguish events characterized by typical values of the excess translational energy $W$ of the fragments with respect to their center-of-mass : (i) $W = 1.14$ eV [3], and (ii) $W = 5.8$ [1] or 6.72 eV [3]. These values correspond to maxima or submaxima in the distribution of the relative velocity $(\gamma)$ in ref. [3], or in the distribution of the relative energy $(W)$ in ref. [1].

The former group of events was ascribed by Seibt [3] to dissociative electronic excitation of N$_2^+$, the latter one to dissociative further ionization of N$_2^+$ to N$_2^{++}$ ; the kinetic energy losses of the primary ions on excitation to the dissociative states involved were evaluated as 3.2 ± 2 eV (former group) and 20.6 ± 3 eV (latter group), and these states proposed to be N$_2^+$(D$^2$ $\Pi_g$) and N$_2^{++}$(A$^3$ $\Pi_u$), respectively [3]. On the other hand, a peak corresponding to a small $W$ and appearing only at a non-zero scattering angle was indicative of the occurrence of an adiabatic dissociation process [3].

From experiments at 2 keV incident energy and by comparison with a rough theoretical model, Moran et al. [4] ascribed the whole velocity spectrum observed in the range $W = 0$ to 7 eV to electronic excitation of N$_2^+$ to the repulsive region of the D$^2$ $\Pi_g$ state.

Studies of the variation of the collision-induced dissociation cross section in the keV energy range with varying energy of the electrons used to produce the primary N$_2^+$ ions [4], [6-8] indicated that this cross section, which is nonzero at threshold, increases with increasing electron energy ; McGowan and Kerwin [6] associated this increase with the population of the A$^2$ $\Pi_u$, the B$^2$ $\Sigma_u^+$, and especially the metastable $^4$ $\Sigma_u^+$ state of N$_2^{++}$ ; the latter state lies about 21 eV above the ground state of N$_2$ ; Moran et al. [4] also observed an increase in the cross section at an electron energy of about 21 eV, Kuprijanov [7] at about 25 and 29 eV, and Wankenne and Momigny [8] at about 20 eV.

Threshold values of the N$_2^+$ ion incident kinetic energy necessary for dissociation to occur on collision with N$_2$ molecules were determined by various workers using ion sources with different electron energies and different ion times of flight [9 - 11]. The discrepancies in their results indicate that metastable states of N$_2^+$ also play a role in the collision-induced dissociation of N$_2^+$ at low incident energies [11]. A lower limit of the energy level of these metastables should be 19 eV above the N$_2$ ground state, since Maier [10] using electrons of energy about 19 eV to produce the N$_2^+$ ions measured a kinetic energy threshold in agreement with what would be expected for a beam of N$_2^+$ in the X$^2$ $\Sigma_u^+$ and/or A$^2$ $\Pi_u$ states only ; again, Comes and Lessmann [12] using a photoionisation source obtained a low-energy collision-

(*) Laboratoire de Physico-chimie des Rayonnements (asso-

(c)iated to the C. N. R. S.), Faculté des Sciences, 91 - Orsay.

(****) Institut d'Electronique Fondamentale (associated to

the C. N. R. S.), Faculté des Sciences, 91 - Orsay.
induced dissociation cross section independent of photon energy up to 19 eV.

Another type of information on the collision-induced dissociation of N2+ ions is brought by the absolute measurement, at high incident energies, of the translational energy of N+ corresponding to the maximum in the distribution recorded at essentially zero angle (this maximum on account of the apparatus collection efficiency function is associated with c. o. m. energies \( W = 0 \)). From such a measurement, performed by comparison of the apparent mass spectrum related to the transition N2+ → N+ with that of the primary N2+ ions, a kinetic energy loss of the primary ions on excitation to the dissociating level was determined by McGowan and Kerwin [2] as 13 ± 5 eV.

The aim of the present work is to cast more light on the mechanisms of the collision-induced dissociation of N2+ ions in the 0.35 to 4.4 keV energy range, by determining the absolute translational energy spectra of N+ from collisions of N2+ on He or Xe under two types of conditions: (i) primary N2+ produced by ionization of N2 by controlled-energy electrons, N+ fragments detected at zero angle, and (ii) primary N2+ produced in a discharge-type ion source, N+ detected at variable angle.

**Experimental.** — The former type of experiment was performed on the apparatus described by Durup, Fournier and Pham [13], the latter on the apparatus built by François, Le Bourhis and Pernot [14], a description of which is given in the companion paper ([15], hereafter referred as paper II).

The apparatus of Durup et al. [13] consists essentially of a 21 cm-radius 60° magnetic-sector mass spectrometer equipped with a Nier-type ion source (Atlas AN-4), a 50 mm-long collision chamber, a parallel-plate condenser for the angular sweeping of the ion beam, and a system of slits which defines the secondary ion beam in a solid angle of 2.5 x 10⁻⁵ steradian. The ionizing electron energy distribution has a full width at half height equal to 0.3 eV. The resolving power of the analyzer is 2 000; an accurate measurement of the ion energy is performed with a differential gaussmeter (Bell 660). The ions are detected by a secondary electron multiplier and the signal is recorded after DC amplification or counted. The time of flight of the ions from the ionization chamber to the collision chamber is 2 x 10⁻⁷ to 10⁻⁶ s. The differential pumping of the analysis section reduces the number of collisions out of the collision chamber to 1%. The pressure in the collision chamber is kept low enough for double collisions to be negligible.

**Results and discussion.** — The following notations will be used throughout the paper.

- \( E_0 \): initial translational energy of the N2+ ions in the laboratory system;
- \( V \): translational energy of the N+ fragment in the laboratory system;
- \( W \): total translational energy of N+ and N with respect to their center-of-mass (c. o. m.)
- \( v \): relative velocity of the fragments N+ + N;
- \( \Delta E \): energy loss of the detected N+ fragment (with respect to \( E_0/2 \));
- \( E^* \): amount of incident translational energy transformed into internal energy of either collision partner;
- \( E_T \): amount of translational energy acquired by the target atom;
- \( V_e \): energy of the electrons used to produce the primary N2+ ions.

\[ 4400 \text{ eV} \text{ N}_2^+ \text{ on He} \]

Figure 1 shows the laboratory energy spectrum of N+ ions detected at zero angle from N2+ on-He collisions at incident energy \( E_0 = 4 \text{ 400 eV} \).

\[ \text{FIG. 1.} \quad \text{Laboratory energy spectrum of N+ from 4 400 eV N}_2^+ \text{ colliding on He (} V \text{ : laboratory energy ; } W \text{ : total c. o. m. energy ; } K \text{ : N+ momentum change).} \]

On this spectrum and on those of figures 3 and 5-8, the maximum which appears at an energy slightly lower than \( E_0/2 \) may be associated with the production of fragments with a total translational energy \( W \) in the c. o. m. system close to zero [13]. The high-energy side of the spectrum arises from forward ejection of the N+ fragment; the low-energy side includes a contribution similar to the high-energy side and due to backward ejection of N+, and peaks or shoulders due to dissociations occuring after the N2+ ion has undergone an energy loss larger than that corresponding to the main maximum of the energy distribution.

In other words, the features of the laboratory energy distribution appearing roughly symmetrically with respect to \( E_0/2 \) and corresponding to a calculated \( W \) independent of \( E_0 \) represent structures in the \( W \) distribution, whereas the features appearing only on the low-energy side of the laboratory energy distribution and with a shift (in laboratory energy) independent of \( E_0 \) represent structures in \( E^* \), amount of translational energy converted into internal energy during the collision.
In the simplest model, which we shall name model 1, the collision is a two-step process, where the \( N^+ \) ions first lose as a whole the sum \( E^* + E_T \) of the internal excitation energy of either collision partner and the translational energy acquired by the target according to momentum conservation, and secondly dissociate. In such a process, if \( W \) is small, the energy \( \Delta E \) lost by \( N^+ \) (with respect to \( E_0/2 \)) equals
\[
\left( E^* + E_T \right)/2.
\]

This process is favoured at high incident energy (low momentum transfer for a given energy loss); it is also favoured when \( E^* \) is only the energy necessary for the excitation of the ion to a dissociative state.

This dissociative state may be reached either by electronic excitation or by adiabatic (vibrational-rotational) excitation or by a combination of these two processes. In the case of an adiabatic excitation a deflection of the c. o. m. of the ion usually will take place [16], so that the fragments will not be observed at small detection angles except if the potential well of the initial electronic state is very shallow.

These models were thoroughly discussed by Cheng et al. [5] who showed that they could not account for their experimental results at low incident energy (\( N_2^+ \)-on-He collisions at \( E_0 = 150 \) eV). They proposed other mechanisms, in particular a stripping mechanism where the molecule ion is first excited to a non-bonding state, then only one of the nitrogen atoms undergoes further interaction with the target, the other one becoming a spectator; this model was found to agree better with experiment [5] than the various forms of model 1. According to such a model, which we shall name model 2, the measured energy loss \( \Delta E \) of \( N^+ \) will include one-half the energy \( \Delta E_1 \) lost by the \( N_2^+ \) ion as a whole, and the energy \( \Delta E_2 \) lost by the \( N^+ \) fragment alone in the second period of the collision. This type of process is likely to be favoured at low incident energy and when a double excitation takes place.

In the following we shall try in first place to interpret the data according to the simplest model (model 1), especially at high \( E_0 \) and low \( \Delta E \). Therefore, unless specified, the given values of \( E^* \) will be calculated according to model 1, i.e. as twice the energy lost by \( N^+ \) minus the translational energy \( E_T \) acquired by the target.

The absolute determination of the translational energy corresponding to the main maximum of figure 1 was performed by using as a marker the primary \( N^+ \) peak and yielded an excitation energy \( E^* = 10 \pm 2 \) eV at \( W = 0 \), in good agreement with the value \( (13 \pm 5 \) eV) obtained by McGowan and Kerwin [2] at lower incident energy.

The energy loss of the ions, the dissociation of which gives rise to the small peak close to the maximum, is \( \Delta E = 16 \pm 1 \) eV, leading to \( E^* = 32 \pm 2 \) eV according to model 1.

The transformation [13], [18] of the spectrum of figure 1 into the distribution of the total translational energy \( W \) in the c. o. m. system yields the most probable \( W \) corresponding to the main peak, \( W = 0.21 \pm 0.03 \) eV, and to the side peak (visible on the l. h. s. of Fig. 1), \( W = 6.2 \pm 0.5 \) eV. The values of \( W \) corresponding to the maxima of the \( v \) distribution \( (1.5 \pm 0.3 \) and \( 6.5 \pm 1 \) eV) are in agreement with the values \( (1.14 \) and \( 6.72 \) eV) obtained by Seibt [3] at \( E_0 = 20 \) keV. The distributions of \( W \) at various incident energies are shown on figure 2; it may be seen that at \( E_0 = 4.4 \) keV the main peak probably consists of two components.

**Fig. 2.** — Total c. o. m. energy distribution of \( N^+ \) from \( N_2^+ \) colliding on He at various incident energies.

Appearance curves (collision-produced \( N^+ \) current vs ionizing electron energy) plotted for particular values of the \( N^+ \) ion translational energy (corresponding to \( W = 0 \) to 6 eV) are straight lines extrapolating to a threshold at 15.8 \pm 0.3 eV.

These results show that the three different phenomena observed (\( W \) close to 0 with \( E^* = 10 \) eV and \( E^* = 32 \) eV; \( W = 6.2 \) eV) are all occurring when the primary \( N_2^+ \) ions are in the ground \( X^2 \Sigma^+_g \) state (energy above \( N_2 \) ground state: 15.6 eV for the vibrational level \( v = 0 \)), and that the dissociation of these ions is the predominant process at \( E_0 = 4.4 \) keV presumably because this state is the most populated one.

Consequently the value \( E^* = 10 \pm 2 \) eV for \( W = 0 \) means that the \( N_2^+ \) ions undergo an excitation to a state lying at 15.6 + 10 \pm 2 = 25.6 \pm 2 \) eV above \( N_2 \) ground state and which is able to dissociate with small excess energy. This state may be the \( D^2 \Pi_g \) state excited above its dissociation limit at 24.3 eV, the \( C^2 \Sigma^+_g \) state if predissociated [19], or other states.
A purely adiabatic (vibrational-rotational) excitation of the $N^+_2$ ions to the continuum of the $X^2 \Sigma_u^+$ state is unlikely to be observed under our conditions (zero scattering angle) owing to the large momentum transfer necessary for this process [16]. On the other hand, electronic excitation of $N^+_2$ to bound levels just under the 24.3 eV dissociation limit on collision with He at 500 eV incident energy was shown in paper II [15] to occur without any vibrational excitation taking place.

The other excitation energy observed

\[ (E^* = 32 \pm 2 \text{ eV}) \]

could be attributed according to model 1 to simultaneous excitation of $N^+_2$ to a dissociative state and of the He target atom to states requiring about 22 eV excitation energy. However, no similar process was observed at incident energies 1-3 keV by Fayeton et al. in II.

A better interpretation of the 32 eV excitation energy in the frame of model 1 is therefore the occurrence of further ionization of $N^+_2$ to $N^+_2^+$ (minimum energy required : 27.2 \( \pm \) 0.5 eV from electron impact data [20]), since it is impossible under our experimental conditions to distinguish $N^+_2^+$ from $N^+$ unless using $^{14}\text{N}^{15}\text{N}$. This interpretation has been confirmed by more recent work performed in Prof. Los' research groupe [21].

Model 2, which would lead to unexplainable values of the energy loss, is besides unlikely to be valid at relatively high $E_0$.

\[ 1 \, 000 \text{ eV } N^+_2 \text{ on He and Xe} \].

Figure 3 shows the recorded distribution of the $N^+$ laboratory energy $V$ for $N^+_2$-on-He collision at incident energy $E_0 = 1 \, 000 \text{ eV}$ and detection at zero angle.

The small peak appearing on the low-energy side of the $V$ distribution corresponds to an excitation energy $E^* = 53 \pm 3 \text{ eV}$.

The transformation of the $V$ distribution into $W$ distribution yields the most probable value $W = 0.27 \pm 0.05 \text{ eV}$.

Figure 4 shows appearance curves, where the ratio of the collision-produced $N^+$ current (for a particular value of $W$) to the parent $N^+_2$ current is plotted against ionizing electron energy for $N^+_2$-on-He and $N^+_2$-on-Xe collisions at the same rare gas pressure in the collision chamber. That ratio is for each $W$ representative of the electron energy dependence of the average cross section for production of fragments with this particular $W$.

For $W = 0$ breaks appear on the appearance curves with both targets but more clearly with Xe, at electron energies $V_e = 21.3 \pm 0.3 \text{ eV}$ and $23.0 \pm 0.5 \text{ eV}$. For $W = 0.4$ and $1.6 \text{ eV}$ the cross section (not shown on Fig. 4 for Xe) is constant with respect to ionizing electron energy.

These results show that metastable $N^+_2$ states, appearing at 21.3 and 23.0 eV and which are of little abundance in the primary ion beam (as apparent on Fig. 10, see later) contribute with a comparatively large cross section to the dissociation processes giving rise to fragments with essentially zero $W$. Possible processes for the dissociation from these states will be discussed in the next section.

It is to be noticed that the cross section for the processes occurring with $N^+_2$ ions in the ground state (which are similar to those observed at $E_0 = 4 \, 400 \text{ eV}$ and may be assigned to electronic excitation to dissociative states) is almost 10 times higher with He than with Xe as a target. In contrast, the cross sections for
the phenomena occurring from the thresholds at 21.3 and 23.0 eV are about the same for both target.

550 eV N$_2^+$ on He and Xe and 350 eV N$_2^+$ on He.

Figures 5 and 6 show laboratory energy spectra of N$^+$ ions from N$_2^+$-on-He collisions at incident energy $E_0 = 550$ eV. The energy resolution $\Delta V$ is better than for higher $E_0$ since the ratio $\Delta V/E_0$ is roughly constant. The curves of figure 5 were obtained with the apparatus of Durup et al. [13] at ionizing electron energies 20 and 30 eV and detection at zero angle ($\pm 0.5^\circ$), the curves of figure 6 with the apparatus of François et al. [14] at a plasma tension of 15 volts and detection at 0$^\circ$ and 3.5$^\circ$. There is a good agreement between the 0$^\circ$ spectra in spite of the quite different types of the two apparatus. Figure 7 is the analogous of figure 5 with Xe instead of He as target gas. Figure 8 is the analogous of figure 6 at $E_0 = 350$ eV and scattering angle 0$^\circ$.

(a) *Main peak.* — The main maximum, which corresponds to a laboratory energy $V$ slightly lower than $E_0/2$, is still to be interpreted as due to dissociation with c. o. m. energy $W = 0$; the shift of this maximum with respect to $E_0/2$ leads to an excitation energy $E^* = 8 \pm 1, 6.5 \pm 1$ and $2.1 \pm 0.5$ eV at $E_0 = 550$ eV and ionizing electron energies $V_e = 20, 22$ and 30 eV, respectively, as shown on
The absolute energy scale is based on the N\(^{+\ +}\) marker. The constancy of the effective potential in the ion source at variable electron energies was tested by checking the constancy of the energy of the primary ions.

**Fig. 9.** Absolute determination of the energy corresponding to the maximum of the laboratory energy spectra of N\(^+\) from 550 eV N\(_2\) colliding on He. From the bottom to the top: N\(^+\) laboratory energy spectra from N\(_2\) produced by electrons of energy \(V_e = 20, 22\) and 30 eV, respectively; N\(^{+\ +}\) « marker » peak.

The peak observed at 30 eV electron energy is very thin, its width at half-maximum corresponding to \(W\) varying from 0 to 0.03 eV.

Appearance curves for N\(_2^+\)-on-He collisions at 550 eV, plotted as collision-produced N\(^+\) current vs ionizing electron energy for various values of N\(^+\) translational energy are shown on figures 10 and 11. Curves 2 and 4, which correspond to \(V = 271\) eV, include a contribution due to \(E^* = 8\) eV, \(W = 0\) (maximum of the distribution at \(V_e \leq 20\) eV, see Fig. 5, 7 and 9) and a contribution due to lower \(E^*\); they present a threshold at \(V_e = 15.6 \pm 0.3\) eV and a break at \(21.2 \pm 0.3\) eV. Curves 1 and 3, which correspond to \(V = 274\) eV, i.e. \(E^* = 2.1\) eV, \(W = 0\) (maximum of the thin peak at \(V_e = 30\) eV, see Fig. 5, 7 and 9) present the same features with an additional strong break at \(V_e = 22.8 \pm 0.4\) eV; this value of \(V_e\) thus appears to be the threshold for the particular process giving rise to that thin peak.

The thresholds at \(21.2 \pm 0.3\) eV and \(22.8 \pm 0.4\) eV are clearly identical with those observed at incident energy \(E_o = 1000\) eV and \(W = 0\) (preceding section).

The threshold at \(21.2 \pm 0.3\) eV may be identified [4] with one of the quartet states of N\(_2^+\) belonging to the \(\{1\ \sigma_g\}^2 \{1\ \sigma_u\}^2 \{2\ \sigma_g\}^2 \{2\ \pi_u\}^2 \{3\ \sigma_g\}^1 \{1\ \pi_g\}^1\)
configuration, e.g. the $^4\Sigma^+_u$ state as apparent on the potential curves reproduced on figure 12 from Gilmore [22]. The values of $W$ corresponding to the dissociation from that state range from 0 to about 0.4 eV (see Fig. 4).

The threshold at 22.8 eV may be identified either with one of the above-mentioned quartet states, e.g. the $^4\Pi_u$ state, or with the $^4\Pi_u$ or the $C^2\Sigma^+_u$, or the $D^2\Pi_u$ state.

Possible processes for the collision-induced dissociation from these states at 21.2 and 23 eV, which occurs with small $W$, are

(i) electronic excitation to states lying just above a dissociation limit (the excitation being favoured with respect to that from the ground $X^2\Sigma^+_g$ state owing to the smallness of the required excitation energy);

(ii) adiabatic (vibrational-rotational) excitation to the continuum of these states (the dissociation products being observed even at zero scattering angle if the potential well is shallow);

(iii) excitation to a predissociating state.

Any of these processes may explain the dissociation from a quartet state at $21.2 \pm 0.3$ eV.

From the observed threshold (22.8 $\pm$ 0.4 eV) and from the observed value of $E^*$, which as above indicated decreases with increasing electron energy down to 2.1 $\pm$ 0.5 eV at $V_e = 30$ eV, it turns out that the upper state involved must dissociate into ground state $N^+$ + N fragments. This upper state is probably a quartet state ($^4\Pi_u$ or $^4\Delta_u$), the initial, state then being another quartet state ($^4\Sigma^+_u$ or $^4\Delta_u$, see Fig. 12) according to spin conservation.

(b) Side peaks. — The first side peak observed on the r. h. s. of figures 5, 6 and 8 is most intense at nonzero scattering angle, as apparent on figure 6; it appears on figure 5 at $0^\circ$ probably because of the poorer angular resolution ($\pm 0.5^\circ$). This peak corresponds to an energy loss $\Delta E = 15.5 \pm 1.5$ eV at $E_0 = 550$ eV and $\Delta E = 21 \pm 2.5$ eV at $E_0 = 350$ eV. Thus, according to model 1, $E^* = 28 \pm 1.0$ eV at $550$ eV and $E^* = 33 \pm 3$ eV at $E_0 = 350$ eV (since $E_T$ is 3 and 9 eV, respectively). Since 8 to 10 eV are required for the dissociative excitation of $N_2^+$, clearly the remainder (19 $\pm$ 4 eV at 550 eV and 24 $\pm$ 6 eV at 350 eV) is used for excitation of the He target. Again model 1 accounts simply for the observed energy loss; model 2 would lead to an unexplainable excitation energy of 10 to 15 eV in addition to the energy necessary for dissociation of $N_2^+$. Further, the energy loss observed at 550 eV, as interpreted according to model 1, is in agreement with the study of non-dissociative excitation of $N_2^+$ on collision with He at 500 eV (paper II [15]): a similar energy loss (30 eV) appears as the sum of an electronic excitation of $N_2^+$ by 8 eV, an excitation of He by 19 eV and the 3 eV translational energy acquired by the target atom.

The disappearance of the peak at zero scattering angle could be interpreted as indicating [16] an adiabatic (vibrational-rotational) excitation of $N_2^+$ to the continuum of the initial state, which from the appearance curve (not shown) is mainly the ground $X^2\Sigma^+_g$ state. However such an interpretation can be rejected from the results described in paper II: the non-dissociative excitation of $N_2^+$ accompanied by He excitation is a purely electronic excitation, and it also has a maximum cross section at a non-zero scattering angle, and a vanishing one at zero angle. Thus dissociative and non-dissociative excitations with $E^* = 30$ to 31 eV appear as related phenomena. The observed deflection of the c. o. m. may be explained simply by the assumption that the transition to $N_2^* + \text{He}^*$ occurs at a pseudo-crossing of the potential curves, which can be reached only at small impact parameter and therefore is associated with a nonzero optimal value of the product incident energy x scattering angle.

The second side peak observed on the r. h. s. of figure 5, 6 and 8 corresponds to an energy loss $\Delta E = 32 \pm 2$ eV at $E_0 = 550$ eV and $\Delta E = 72 \pm 4$ eV at $E_0 = 350$ eV.
Taking into account the translational energy $E_T$ acquired by the target, one obtains the following values of the inelastic energy loss according to model 1:

$$E^* = 53 \pm 3, 50 \pm 3 \text{ and } 43 \pm 3 \text{ eV at } E_0 = 1000, 550 \text{ and } 350 \text{ eV, respectively.}$$

The appearance curve (Fig. 10) shows that the process under consideration occurs mainly with $N_2^+$ ions initially in the ground $X^2 \Sigma_g^+$ state. Therefore, the energy $E^*$ necessary for dissociation would be about 9 eV. Thus, the observed values of $E^*$ do not correspond to the sum of the dissociation energy of $N_2^+$ and an excitation energy of He. They may be the sum of the ionization energy of $N_2^+$, 27.2 $\pm$ 0.5 eV [20], (since we do not distinguish $N_2^{++}$ from $N^+$) and an excitation energy of He equal to 26, 23, 3 and 16 $\pm$ 3 eV at $E_0 = 1000, 550$ and 350 eV, respectively.

It is interesting to notice that in the interpretation according to model 1 the amount of incident translational energy converted into internal energy of either reactant equals 42 $\%$, 73 $\%$ and 98 $\%$ of the total translational energy available in the c. o. m. system at $E_0 = 1000, 550$ and 350 eV, respectively.

Now the observed energy losses can very well be accounted for on the basis of model 2, viz. a two step process where firstly the $N_2^+$ ion is excited as a whole (by about 9 eV) to a dissociative state and secondly the $N^+$ fragment only interacts further with the He target which then undergoes an excitation by an amount equal to 23.4 $\pm$ 1.5, 25 $\pm$ 2 and 26 $\pm$ 2 eV at $E_0 = 1000, 550$, and 350 eV, respectively.

This latter interpretation appears to be the more likely since (i) the derived excitation energies are close to one another at the different $E_0$, in contrast with those derived from model 1, and (ii) model 2 may account for the width of the observed peak, whereas in the case of model 1 where as shown above no dissociation but only further ionization of $N_2^+$ would take place a thin peak is to be expected as that observed in the 4 400 eV experiment (see above, Fig. 1).

Further experiments would be necessary for deciding among the two models. In any case, the large amount of translational energy converted into internal energy, and the fact that the process under consideration shows up at relatively low incident energies are conclusive evidences for a transition occurring at a pseudocrossing of potential surfaces.

Conclusions. — Various collision-induced dissociation processes were observed.

(i) An electronic excitation occurring mainly from the ground $X^2 \Sigma_g^+$ state, requiring from 8 $\pm$ 1 eV (at $E_0 = 500$ eV) to 10 $\pm$ 2 eV (at $E_0 = 4400$ eV), and leading to a state which is able to dissociate with zero excess c. o. m. energy. This state which therefore dissociates into the $N^+(3P)$ and $N(4S^0)$ fragments, whose energy is 24.3 eV above $N_2^+$ ground state, lies itself at about the same energy; it is most probably the $D^2 \Pi_g$ state or a predissociated doublet state (e. g., $C^2 \Sigma_g^+$), according to spin conservation rules.

(ii) Two electronic excitation processes also occurring from the ground $X^2 \Sigma_g^+$ state, especially at high incident energy and giving rise to large $W's$ (typically 1.3 and 6.2 eV, respectively), in agreement with Seibt's results [3].

(iii) An electronic or vibrational-rotational excitation from a quartet state of $N_2^+$ lying at 21.3 $\pm$ 0.3 eV (above $N_2^+$ ground state) to a state dissociating with separation energies $W$ ranging from 0 to about 0.4 eV.

(iv) An electronic excitation from another quartet state, lying at 22.8 $\pm$ 0.4 eV, to a state dissociating to the $N^+(3P) + N(4S^0)$ fragments with a separation energy $W \leq 0.03$ eV.

(v) An electronic excitation towards a dissociative state occurring mainly from the ground $X^2 \Sigma_g^+$ state, with simultaneous excitation of the helium target, in a collision at small impact parameter and low incident energy (observed at $E_0 = 350$ and 550 eV).

(vi) A process probably similar to (v) but occurring along a different path and observed at $E_0 = 350$, 550 and 1000 eV.

The latter two processes are most easily interpreted as transitions taking place through potential surface crossings.

Acknowledgements — The authors are indebted to Dr M. Barat, Dr J. Baudon and Miss J. Fayeton for many fruitful discussions. One of the authors (P. F.) was able through his present collaboration with Professor J. Los and Dr J. Schopman to verify the interpretation of some of the reported data.

References

[7] Tikhomirov (M. V.), Komarov (V. N.) and Tunicki (N. N.), Zh. fiz. Khim., 1964, 38, 955;


    FRANÇOIS (R.), LE BOURHIS (G.) and PERNOT (A.),
    Rapport Interne, Institut d'Electronique Fondamentale, Orsay, 1970 ;

    FAYETON (J.), PERNOT (A.), FOURNIER (P.) and BARAT, (M.), submitted to J. Physique (referred as paper II in the text).

[16] For experimental and theoretical evidence pertinent to the correlation between vibrational-rotational excitation of the ion and deflection of its c. o. m., see references [15] and [17], respectively.


[21] FOURNIER (P.), SCHOPMAN (J.), VAN DE RUNSTRAAT (C. A.), LOS (J.), to be published.