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THE DISSOCIATIVE ELECTROIONIZATION OF NITROUS OXIDE. THE O^+ DISSOCIATION CHANNEL

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ABSTRACT

By electroionization mass spectrometry and ion kinetic energy analysis, the O^+ fragment ion formation from N_2O has been analysed. Different appearance energies are measured and interpreted. Between the onset at 15.27 eV and 22 eV only two dissociation limits are involved, i.e., $O^+(^4S)+N_2(X^1\Sigma_g^+)$ at 15.29 eV and $O+(^2D)+N_2(X^1\Sigma_g^+)$ at 18.61 eV. In both cases, $N_2(X^1\Sigma_g^+)$ is produced in its v = 0 up to v = 8 vibrational levels. Predissociation of ionic and Rydberg states of N_2O are the dominant processes.

INTRODUCTION

A detailled study of the dissociative electroionization of nitrous oxide leading to N^+_2 and NO^+ fragment ions has recently been achieved (1). As these fragments formation has been abundantly studied, much less attention has been payed to the dissociation channels producing O^+ and N^+ . The aim of this contribution is to present the preliminary results on the O^+ production from N_2O. The work on N^+ is still in progress.

EXPERIMENTAL RESULTS

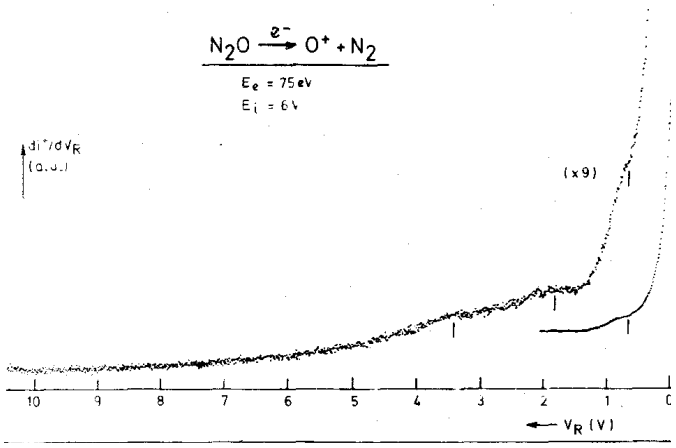
The experimental set-up and the usual experimental conditions in this electron impact experiment are fully described elsewhere (2). The most striking features are (i) the analysis of ions energies by a retarding field before mass analysis and (ii) the recording of the first differentiated retarding and ionization efficiency curves.

A typical O^+ ion translational energy distribution, as observed for 75 eV electrons is shown in Fig. 1. Beside the major thermal peak, maxima are observed at 0.064 eV, 1.70 eV and 3.34 eV.

First differentiated ionization efficiency curves of O recorded at different retarding potential settings are shown in Fig. 2. Thresholds are determined at (15.27±0.18) eV, (15.83±0.17) eV and (19.56±0.3) eV. Maxima related to autoionization are measured at (17.53±0.17) eV and at about 23.5 eV.

By plotting the onsets measured for retarding potential setting scanned from 0-2.5 eV, the diagram shown in Fig. 3 is obtained.

Fig. 1. *First differentiated retarding curve for O^+/N_2O at 75 eV electron energy.*



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DISCUSSION

For clarity we will briefly discuss each portion of the diagram shown in Fig. 3 and numbered 1 to 10.

1. The onset at (15.27 ± 0.18) eV is very close to the thermodynamical threshold of 15.29 eV calculated for

$$N_2O + e^- \rightarrow O^+(^4S) + N_2\,(X^1\,\Sigma_g^+) + 2e^- \quad (1)$$

This process has to occur by predissociation of the $\tilde{X}\,^2\Pi$ state (populated via autoionization) through the $^4\Sigma^-$ repulsive state. The excess energy is entirely converted into translational energy of the fragments.

2. At (15.83 ± 0.17) eV the same reaction (1) is involved, but the N_2 fragment appears in the v = 2 level.

3. Between 16.5-19.2 eV, corresponding to the ionization of the $\tilde{A}^2\Sigma^+$ and $\tilde{B}^2\Pi$states of N_2O, the O^+ ions are formed at least by predissociation of these states by the $^4\Sigma^-$ state. The slope of segment (3) indicates that N_2 $(X^1\Sigma^+)$ is formed between v = 0-8.

4. From 19.5-20 eV the straight line extrapolates to 17.6 eV. The energy balance shows that only translational energy is involved and the N_2 fragment remains in the v = 8 level. Rydberg states of $N_2O$and the $\tilde{C}\,^2\Sigma^+$ state of N_2O^+ are predissociated by the $^4\Sigma^-$ state.

5. The peak at 17.5 eV in the ionization efficiency curve of O^+ is due to autoionization. O^+ ions are produced at low kinetic energy and N $(X^1\,\Sigma_g^+)$ is in its v = 8 level.

Fig. 2. *First differentiated ionization efficiency curve of O^+ /N_2O at different retarding potential settings (V_R).*

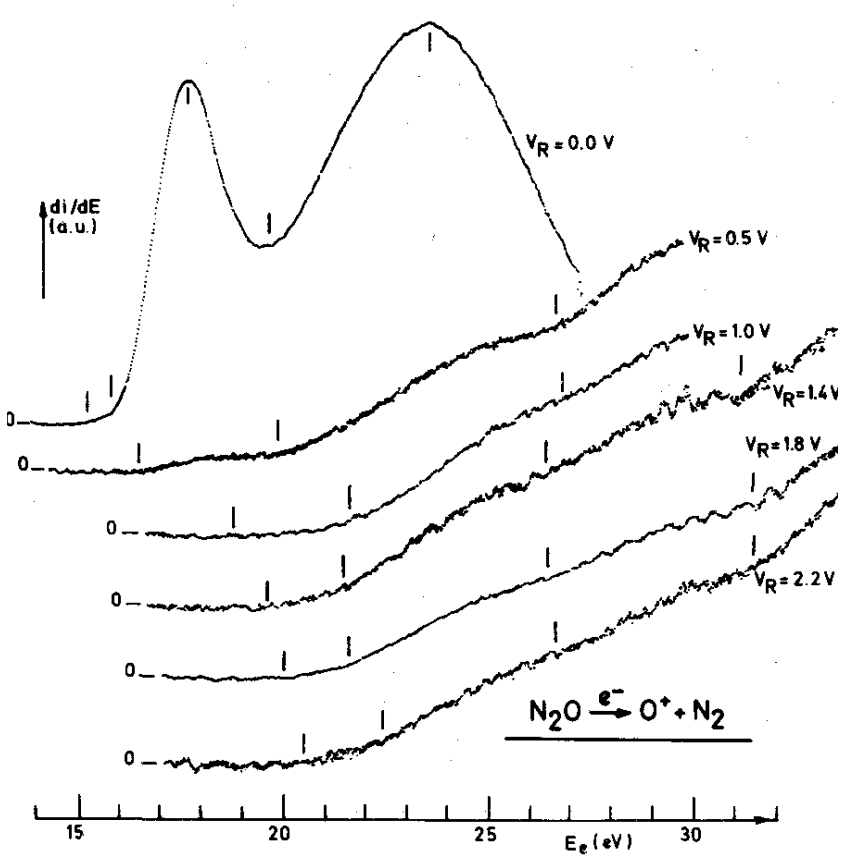

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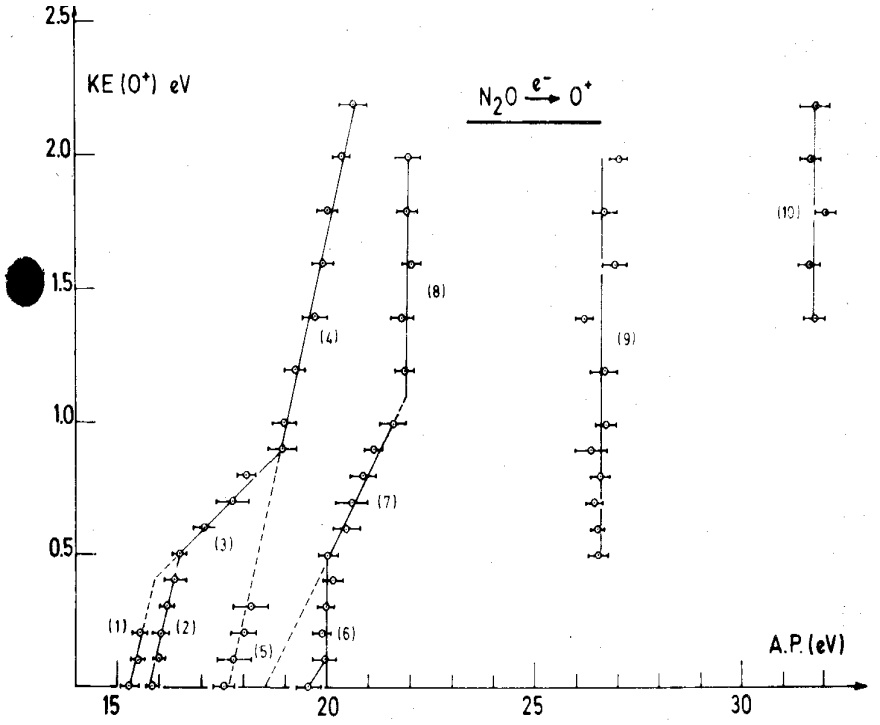
Fig. 3. *Appearance energy-versus-kinetic energy diagram of O^+ /N_2O.*



6. The threshold at (19.56 ± 0.3) eV corresponds to the process

$$N_2O + e^- \rightarrow N_2(X^1\Sigma_g^+, v = 3) + O(^2D) + 2e^- \qquad (2)$$

7. The segment extending from 20-21.7 eV extrapolates to 18.5 eV in close agreement with the threshold calculated for the limit N_2 ($X^1\Sigma_g^+$) + $O(^2D)$ at 18.6 eV. The slope indicates the formation of N_2 in its v = 2-5 levels. This would occur through predissociation of the $\tilde{C}\,^2\Sigma^+$ state of N_2O^+ and Rydberg states by a repulsive $^2\Pi$ state. This state has been calculated by Lorquet and Cadet (3).

8-10. The vertical bars at 21.9 eV, 26.6 eV, and 31.7 eV are dissociations leading to O^+ through predissociation of doubly excited states of NO^+. These were previously identified (4,5).

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