

Appearance Potentials and Kinetic Energies of Ions from N₂, CO, and NO

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A recently developed method has permitted the measurement of excess translational energy of ions formed in a time-of-flight mass spectrometer. The method, in conjunction with the RPD technique for determining appearance potentials, has been applied to the electron-impact study of nitrogen, carbon monoxide, and nitric oxide. A total of 31 different ionization processes have been observed and identified, several of which had not been previously reported in the literature.

INTRODUCTION

One of the principal applications of mass spectrometry is the study of ionization and dissociation produced by electron impact. In order to draw meaningful conclusions from the data, it is necessary to determine experimentally (1) the appearance potential of the ion; (2) any excess energy the ion possesses as its appearance potential; and (3) the identity (m/e) of the ion. Of the various techniques proposed for the experimental determination of appearance potentials, the RPD method developed by Fox and co-workers^{1,2} has proven one of the most reliable. Moreover, it has often proved possible to correlate breaks in RPD ionization efficiency curves with the onset of additional ionization processes in which the products are formed in electronically excited states. Recently, a technique has been proposed³ for the measurement of initial translational energies of ions formed by dissociation ionization in a time-of-flight mass spectrometer. It was shown that for ions with a quasithermal energy distribution the average translational energy is given by

$$\bar{V} = (N_0/3.69) (qE_s)^2 [(W_{1/2})^2/M], \quad (1)$$

where N_0 is Avogadro's number, q is the charge on the ion, E_s is the magnitude of the drawout pulse, $W_{1/2}$ is the full width of the ion peak at half-maximum (seconds), and M is the mass of the ion in amu. Likewise, the maximum initial translational energy is given by

$$U_0 = \frac{1}{8} N_0 (qE_s)^2 [(W_0)^2/M], \quad (2)$$

where W_0 is the full width of the ion peak at its base (seconds). The present work applied this method, in conjunction with the RPD method of determining appearance potentials, to a study of the dissociative ionization of three diatomic molecules for two reasons: first, to demonstrate the utility of these techniques in such studies; and second, to attempt to clarify certain inconsistencies that have arisen in previous investigations of these molecules as well as to observe and

identify additional ionization processes not previously reported.

EXPERIMENTAL

The instrument used in the present investigation, a Bendix Model 12 time-of-flight mass spectrometer, and the method of measuring translational energies have been described elsewhere.³ The ion lens was not used when determining peak shapes, but it was used to obtain maximum intensity in appearance potential measurements. Likewise, the gate pulse was made as narrow as possible (20 nsec) to improve resolution for the determination of peak shapes, but a wider gate pulse was used to give greater intensity for appearance potential measurements.

The appearance potentials of all major ions were determined by the RPD technique of Fox. A five-grid electron gun was employed and a ΔV_R of 0.1 eV was used. Argon or neon, whichever had an ionization potential closer to that of the ion under investigation, was used to calibrate the electron energy scale. Because of their low intensity, the appearance potentials of the doubly charged atomic ions (N²⁺, O²⁺, and C²⁺) were determined by a variation of the energy compensation method.⁴ The partial pressure of neon was adjusted until the intensity of Ne²⁺ at 100 eV was equal to that of the ion under investigation. The appearance potential was taken as that electron energy at which the intensity had decreased to 0.1% of its value at 100 eV. The appearance potentials of the negative ions were determined by slowly increasing the electron energy until the ion under investigation first appeared on the oscilloscope. Some SF₆⁻ was used to calibrate the electron energy scale for negative ions. In all cases, the appearance potentials reported represent the average of at least five trials, and the uncertainty reported is the standard deviation.

The excess translational energies of the fragment ions were determined from an analysis of the peak shapes, as described elsewhere.³ The excess energy was plotted as a function of the electron energy and extrapolated to the appearance potential. Because of low ion intensity near the ionization potential, it was usually necessary to extrapolate such a curve over a distance of 1 or 2 V (of electron energy). The uncertainty reported

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¹ R. E. Fox, W. M. Hickam, D. J. Grove, and T. Kjeldaas, *Rev. Sci. Instr.* **26**, 1101 (1955).

² R. E. Fox, W. M. Hickam, T. Kjeldaas, and D. J. Grove, *Phys. Rev.* **84**, 859 (1951).

³ J. L. Franklin and P. M. Hierl, *J. Chem. Phys.* **47**, 3148 (1967), preceding paper.

⁴ R. W. Kiser and E. J. Gallegos, *J. Phys. Chem.* **66**, 947 (1962).

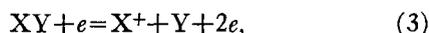
with the translational energies represents an estimated maximum error arising from such a procedure.

Since only atoms or atomic ions were formed with excess translational energy in this study we have employed kinetic and translational energy as synonymous. Obviously this would not apply to polyatomic species.

High-purity tank nitrogen, carbon monoxide, and nitric oxide gas were used without further purification in these studies.

RESULTS AND DISCUSSION

If, in the dissociative ionization of the diatomic molecule XY



the ion X^+ is observed to be formed with excess translational energy, $U(X^+)$, at its appearance potential $A.P.(X^+)$, it is convenient to define, by the following equation, the appearance potential corresponding to the formation of the products with zero velocity at infinite separation:

$$A.P._0(X^+) = A.P.(X^+) - [(m_X + m_Y)/m_Y]U(X^+), \quad (4)$$

where m_X and m_Y are the masses of Atoms X and Y, respectively. It can easily be shown, then, that

$$A.P._0(X^+) = D(X-Y) + I.P.(X) + E(X^+) + E(Y), \quad (5)$$

where $D(X-Y)$ is the bond strength of the molecule XY, $I.P.(X)$ is the ionization potential of the atom X, and $E(X^+)$ and $E(Y)$ represent the excess electronic energy of the products if they are formed in other than their ground electronic states.

Nitrogen

A typical ionization efficiency (I.E.) curve for the production of N_2^+ is shown in Fig. 1. Onset occurred at 15.59 ± 0.05 eV, with breaks occurring at 16.87 ± 0.10 , 18.75 ± 0.20 , and 23.86 ± 0.20 eV. The first two breaks are sharp and undoubtedly represent the onset of new

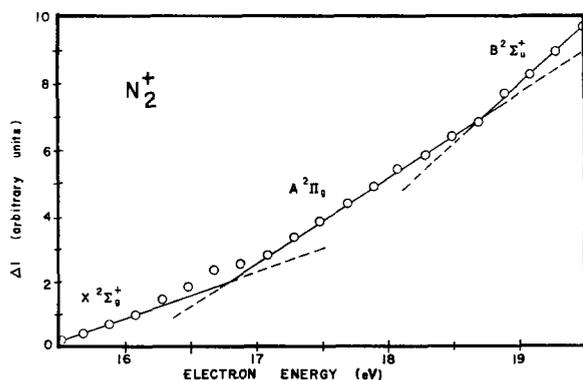


FIG. 1. Ionization efficiency curve for the production of N_2^+ from nitrogen.

TABLE I. Ionic processes in N_2 .

Process	Products	A.P. (eV)		
		This work	Previous studies	Spectroscopic
1	$N_2(X^2\Sigma_g^+)$	15.59 ± 0.05	15.7 ^a 15.60 ^b 15.60 ^c 15.63 ^d	15.58 ^j
2	$N_2(A^2\Pi_u)$	16.87 ± 0.10	16.71 ^b 16.93 ^c 16.84 ^d	16.69 ^k
3	$N_2^+(B^2\Sigma_u^+)$	18.75 ± 0.20	18.60 ^b 18.84 ^c 18.76 ^d	18.75 ^k
4	$N_2^+(C^2\Sigma_u^+)$	23.86 ± 0.20	23.53 ^d	23.58 ^k
5	$N_2^{2+}(b^1\pi_u)$ or $(^3\Sigma_g^-)$	44.2 ± 0.5	42.7 ^e 43.5 ^f 43.8 ^g	43.8 ^l
6	$N^+(^3P) + N(^4S)$	24.32 ± 0.03	24.35 ^g 24.32 ^h 24.3 ^a	24.30 ^m
7	$N^+(^3P) + N(^2D)$	26.65 ± 0.15	26.71 ^g 26.7 ⁱ 26.66 ^h	26.68 ^m
8	$N^+(^3P) + N(^2P)$	28.0 ± 0.2	28.1 ^g 27.93 ^h	27.88 ^m
9	$2N^+(^3P)$	39.0 ± 2.0	...	38.84 ^m
10	$N^{2+}(^3P) + N(^4S)$	53.6 ± 1.0	...	53.9 ^m

^a Reference 13.

^b R. E. Winters, J. H. Collins, and W. L. Courchene, Paper presented at the 14th Annual Conference on Mass Spectrometry and Allied Topics, Dallas, Tex., May, 1966.

^c R. E. Fox and W. M. Hickman, *J. Chem. Phys.* **22**, 2059 (1954).

^d D. C. Frost and C. A. McDowell, *Proc. Roy. Soc. (London)* **A232**, 227 (1955).

^e A. C. Hurley and V. W. Maslen, *J. Chem. Phys.* **34**, 1919 (1961).

^f F. H. Dorman and J. D. Morrison, *J. Chem. Phys.* **35**, 575 (1961).

^g Reference 5.

^h Reference 12.

ⁱ Reference 11.

^j G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules*. (D. Van Nostrand Co., Inc., New York, 1950), 2nd ed.

^k A. B. Meinel, *Astrophys. J.* **114**, 431 (1951).

^l Reference 9.

^m Calculated assuming $D(N_2) = 9.76$ eV (5, 11). Ionization potentials and electronic energy levels are from Ref. 12.

processes. The one at 23.86 eV is somewhat less certain, although it does correspond to a known state of N_2^+ . These results are interpreted in Table I, where they are also compared with the results obtained by other workers. The curvature of the ionization efficiency curve (Fig. 1) in the region 16.2 to 17.2 eV was observed in each of the trials. Such a deviation from linearity in the general region 16.0 to 17.5 eV has also been observed by other workers.⁵⁻⁸ It has been explained⁵ as representing excitation to various vibrational levels of the ionized molecule.

⁵ E. M. Clarke, *Can. J. Phys.* **32**, 764 (1954).

⁶ R. E. Fox, *J. Chem. Phys.* **35**, 1379 (1961).

⁷ Y. Kaneko, *J. Phys. Soc. (Japan)* **16**, 1587 (1961).

⁸ J. D. Morrison, Annual Conf. Mass Spectrometry Allied Topics 12th ASTM Committee E-14 on Mass Spectrometry, Montreal, Canada, 7-12 June 1964.

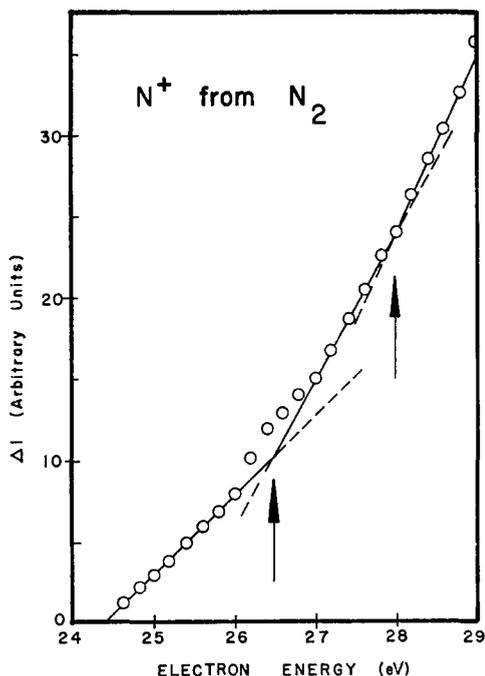


Fig. 2. Ionization efficiency curve for the production of N^+ from nitrogen.

The doubly charged molecular ion N_2^{2+} was observed to have an appearance potential of 44.2 ± 0.5 eV. This value must be considered uncertain, however, because of the high background at m/e 14.5 from the incompletely resolved peaks at 14 and 15. From potential-energy curves calculated by Hurley,⁹ the observed appearance potential could be interpreted as representing ionization to either the $b^1\pi_u$ state or the $^3\Sigma_g^-$ state of N_2^{2+} , both of which pass through the Franck-Condon region about 44 eV above the ground state.

Figure 2 shows a typical ionization efficiency curve for N^+ from N_2 . Onset occurred at 24.32 ± 0.03 eV, in good agreement with the spectroscopically determined dissociation limit of 24.30 eV.¹⁰ There was a definite break in the I.E. curve at 26.2 eV. The curved portion in the region 26.2 to 26.6 eV is almost identical to that observed by Burns¹¹ and interpreted by him as representing the onset of a process by which the N^+ ion is formed in an excited state. This curvature, however, was not observed by Clarke,⁵ using a velocity selector, nor was it observed by Frost and McDowell,¹² who repeated Burns' RPD experiments in order to clear up this discrepancy. Although this anomalous curvature occurred in each of the five appearance potential measurements on N^+ , and although it appears to be identical in shape to that reported by Burns,¹¹ it is not believed to be caused by the onset of a new process forming excited N^+ ions, as Burns claimed. The irregu-

lar curvature is not consistent with such an interpretation, nor could this explain the failure of Frost and McDowell¹² to observe such a process. It is possible that the curvature arises from some autoionization process.

Ignoring the curvature and extrapolating the linear segment of the I.E. curve, there is clearly a break occurring at 26.65 ± 0.15 eV and with less certainty, there appears to be one at 28.0 ± 0.2 eV. Such breaks have been observed in all previous investigations of the dissociative ionization of nitrogen with monoenergetic electrons.^{5,11,12} In agreement with previous results,^{13,14} N^+ was found to be formed with no excess translational energy at 24.3 eV (see Fig. 3). It is assumed that no appreciable excess energy is associated with the processes occurring at 26.65 and 28.0 eV, the observed appearance potentials agree well with those calculated for Processes 6 through 8 in Table I.

Information concerning the state of the N_2^+ ion which gives rise to the observed dissociation products can be inferred from the translational energy data. As shown in Fig. 3, N^+ ions are formed with no excess translational energy at the appearance potential, which indicates that the turning point of the dissociation asymptote lies within the effective Franck-Condon

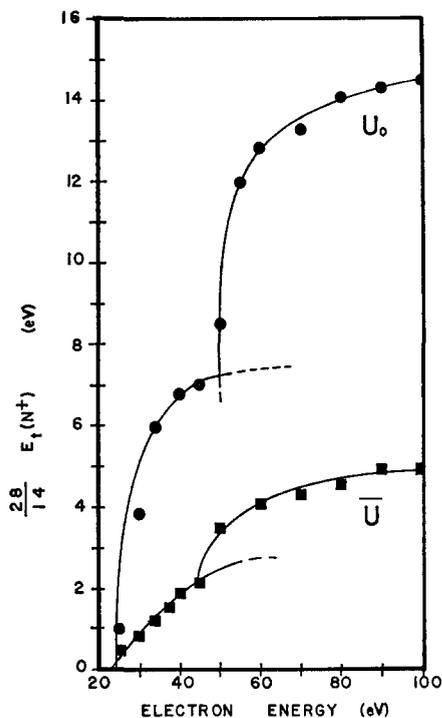


Fig. 3. Total excess translational energy vs electron energy for the dissociative ionization of nitrogen. \bar{U}_0 represents the maximum translational energy, while \bar{U} is the average excess translational energy.

⁹ A. C. Hurley, *J. Mol. Spectry.* **9**, 18 (1962).

¹⁰ A. E. Douglas, *Can. J. Phys.* **30**, 302 (1952).

¹¹ J. F. Burns, *J. Chem. Phys.* **23**, 1347 (1955).

¹² D. C. Frost and C. A. McDowell, *Proc. Roy. Soc. (London)* **236**, 278 (1956).

¹³ H. D. Hagstrum, *Rev. Mod. Phys.* **23**, 185 (1951).

¹⁴ R. J. Kandel, *J. Chem. Phys.* **22**, 1496 (1954).

region. As the electron energy is increased, however, the total translational energy of the fragments increases and levels off at an average value of about 2 eV. This indicates that, at an internuclear distance equal to the equilibrium internuclear distance of the nitrogen molecule, the potential-energy curve for the N_2^+ state involved lies about 2 eV above the dissociation asymptote. A set of potential-energy curves for various states of the N_2^+ ion has been calculated by Gilmore.¹⁵ These calculated curves indicate that the N^+ ion observed at 24.3 eV probably does not arise from any of the first three levels of the N_2^+ ion. The $c^2\Sigma_u^+$ state, which McDowell¹⁶ thinks is responsible for the production of the N^+ ions, has the proper shape in the Franck-Condon region but does not dissociate to the products formed at 24.3 eV. It does, however, correlate with the products observed at 26.7 eV and very possibly could be the state of the N_2^+ ion which dissociates according to Process 7 in Table I. While these curves are not complete enough to answer the question unambiguously, it seems possible that a state such as the $D^2\pi_g$ state is the one which gives rise to the products observed at 24.3 eV. The failure to observe the formation of the N^+ ion in its first excited state (1D) has been explained¹⁷ by the fact that, according to the Wigner-Witmer correlation rules, such dissociation products correlate only with quartet states, but no quartet states of N_2^+ have been observed spectroscopically.

As shown in Fig. 3, there is a sudden and sharp increase in the translational energy of the fragments at an electron energy of 48 ± 2 eV. This sudden increase was interpreted as resulting from the onset of a process by which two N^+ ions are formed simultaneously by the decomposition of an unstable N_2^{2+} ion.¹⁸ A sharp increase in the efficiency of production of N^+ ions at electron energies of 47 to 50 eV has been reported by other workers.^{19,20} Moreover, according to Hurley's calculations,⁹ there is a state ($A^3\pi_g$) of the N_2^{2+} ion which passes through the Franck-Condon region in such a manner that dissociation into two $N^+(^3P)$ ions should occur at about 46.5 eV. If his postulated dissociation products are correct, the ions should be formed with a minimum of 8-eV total kinetic energy, which is what the present measurements (based upon U_0) indicate. Consequently, a fourth process (9 of Table I) has been postulated for the formation of N^+ ions from nitrogen.

The appearance potential of the N^{2+} ion was found to be 63.63 ± 0.20 eV. The ion was observed to be formed with 5.0 ± 0.4 eV of translational energy at the

appearance potential. Assuming that the bond strength is 9.76 eV¹¹ and that 44.15 eV are required to remove two electrons from an N atom,²¹ Eq. (1) indicates that the sum of the excess electronic energy is -0.3 ± 1.0 eV. Since the first excited state of the N atom is 2.4 eV above the ground state, while the first excited state of the N^{2+} is about 7 eV above the ground state, it would appear that in the observed process both products are formed in their ground electronic states (see Process 10, Table I).

Carbon Monoxide

The appearance potentials measured for CO^+ are listed in Table II. The present data agree well with previous electron-impact data, which, in turn, agree well with spectroscopic values.

It was not possible to obtain an accurate value for the appearance potential of CO^{2+} because of the background at m/e 14 due to nitrogen ions resulting from a small air leak.

The negative ion O^- was observed to be formed by a resonance process, with onset occurring at 9.7 ± 0.2 eV. The width of the ion peak seemed to indicate that the ion was formed with excess translational energy. However, it was found that all negative ion peaks were unusually wide, even those for ions which are known to possess little or no excess translational energy. The conclusion was that translational energy measurements could not be made on negative ions, at least under the present conditions. If, however, it is assumed that the O^- ions are formed with little or no excess translational energy, the observed appearance potential of 9.7 eV agrees very well with the value of 9.63 eV calculated for Process 3, shown in Table II, assuming $E.A.(O) = 1.48$ eV.²²

The ion O^- was also observed to be formed by an ionic dissociation process with onset occurring at 20.9 ± 0.2 eV. Since this value agrees very well with the value of 20.82 ± 0.05 eV observed for the appearance potential of the C^+ ion, it is concluded that these ions were formed simultaneously by the ion-pair process shown in Table II.

The ionization efficiency curve for C^+ (Fig. 4) shows a sharp increase in the production of C^+ at 22.45 ± 0.10 eV. The ions were observed to be formed with zero translational energy at this appearance potential, which agrees with the results of previous investigators.^{19,23}

The negative ion C^- was observed to appear at 23.3 ± 0.1 eV in agreement with the findings of Chupka and Inghram.²⁴ It is concluded that these ions are formed by the same process as that yielding O^+ ions at 23.20 ± 0.05 eV. The results obtained for the O^+ ion,

¹⁵ F. G. Gilmore, *J. Quant. Spectry. Radiative Transfer* **5**, 369 (1965).

¹⁶ C. A. McDowell, *Applied Mass Spectrometry* (The Institute for Petroleum, London, 1954), pp. 129-153.

¹⁷ F. H. Field and J. L. Franklin, *Electron Impact Phenomena* (Academic Press Inc., New York, 1957).

¹⁸ J. T. Tate, P. T. Smith, and A. L. Vaughan, *Phys. Rev.* **48**, 525 (1935).

¹⁹ H. D. Hagstrum and J. T. Tate, *Phys. Rev.* **59**, 354 (1941).

²⁰ A. L. Vaughan, *Phys. Rev.* **38**, 1687 (1931).

²¹ C. E. Moore, *Natl. Bur. Std. Circ. No. 467* (1949).

²² L. M. Branscomb and S. J. Smith, *Phys. Rev.* **98**, 1127 (1955).

²³ C. E. Berry, *Phys. Rev.* **78**, 597 (1950).

²⁴ W. A. Chupka and M. G. Inghram, *J. Phys. Chem.* **59**, 100 (1959).

TABLE II. Ionic processes in CO.

Process	Products ^a	A.P. (eV)		
		This work	Previous studies	Spectroscopic
1	CO ⁺ (X ² Σ _v ⁺)	14.00±0.05	14.1 ^b 14.05 ^c 13.98 ^d	14.009 ^e
2	CO ⁺ (A ² π _u)	16.5±0.1	16.4 ^d	16.53 ^e
3	O ⁻ (² P)+C(³ P)	9.7±0.2	9.6 ^b 9.5 ^e	9.63 ^f
4	{O ⁻ (² P)+C ⁺ (² P)} {C ⁺ (² P)+O ⁻ (² P)}	20.9±0.2 20.82±0.05	21.1 ^b 20.9 ^b	20.89 ^f
5	C ⁺ (² P)+O(³ P)	22.45±0.10	22.8 ^b	22.37 ^f
6	{O ⁺ (⁴ S)+C ⁻ (⁴ S)} {C ⁻ (⁴ S)+O ⁺ (⁴ S)}	{23.20±0.05} {23.3±0.1 }	23.2 ^b	23.22 ^f
7	O ⁺ (⁴ S)+C(³ P)	24.65±0.05	...	24.72 ^f
8	O ⁺ (⁴ S)+C(¹ D)	26.00±0.10	...	25.99 ^f
9	O ⁺ (⁴ S)+C(¹ S)	27.45±0.10	...	27.40 ^f
10	O ⁺ (² D)+C(³ P)	28.0±0.1	...	28.04 ^f
11	C ²⁺ (¹ S)+O(³ P)	46.0±1.1	...	46.75 ^f
12	O ²⁺ (⁴ S)+C(³ P)	59.7±1.0	...	59.87 ^f

^a The appearance potential was measured upon the first ion given; i.e., the one on the left when two are formed.

^b Reference 13.

^c See Ref. b of Table I.

^d See Ref. c of Table I.

^e See Ref. j of Table I.

^f Calculated assuming $D(\text{CO}) = 11.11$ eV [see C. R. Lagergren, Dissertation Abstr. 16, 770 (1956)]. E.A.(O) = 1.48 eV,²² and E.A.(C) = 1.5 eV [see H. S. W. Massey, *Negative Ions* (Cambridge University Press, Cambridge, England, 1950)]. Ionization potentials and electronic energy levels from Ref. 21.

however, are in complete disagreement with the previously published results of Hagstrum¹⁹ and of Berry,²³ who reported that very few, if any, O⁺ ions with less than 0.65 eV of excess translational energy were formed, and that appreciable numbers were formed with more than 2.5 eV. The present investigation, on the other hand, indicates that the average excess translational energy of the O⁺ ions is zero at the appearance potential. Moreover, appearance potentials calculated on the assumption of zero excess translational energy agree very well with the experimental values determined in this investigation (Table II). A typical ionization efficiency curve for the production of O⁺ from CO is shown in Fig. 5. The breaks at 24.65, 26.0, and 28.0 eV are quite definite; the one at 27.45 eV is less so, but is in very good agreement with known states according to Process 9.

The possibility of the simultaneous formation of C⁺ and O⁺ from an unstable CO²⁺ was investigated. As pointed out by Vaughan,²⁰ 35.98 eV are needed to form the two singly charged atomic ions in their ground states, while the minimum energy required to form CO²⁺ is about 43 eV. This would result in dissociation products with a total translational energy of about 7 eV, assuming the products to be in their ground states. By conservation of momentum, the C⁺ ion would have 4 eV of energy, while the O⁺ ion would have 3 eV.

As indicated in Fig. 6, the observed maximum translational energies were 1.2 and 0.8 eV for the O⁺ ion and the C⁺ ion, respectively. The observed energies are much lower than would be expected for the hypothetical process. Even if one assumes that part of the 7.0 eV of excess energy is used to form excited electronic states of the product ions, one would still expect, by conservation of momentum, that the C⁺ ion would have more translational energy than the O⁺ ion if they were produced by the dissociation of CO²⁺. Since this is not the case, it is concluded that this process did not occur. This finding is in agreement with the conclusion reached by Vaughan.²⁰

The C²⁺ ion was observed to be formed with 4.7±0.5 eV of excess translational energy at its appearance potential, 54.2±0.2 eV. These results indicate that the sum of excess electronic energy is -0.8±1.1 eV. Thus, it appears that the products are both formed in their ground electronic states, since the first excited level, the ¹D level of atomic oxygen, is 1.97 eV above the ground state.

A similar conclusion is drawn for the ion O²⁺, which was observed to appear with 0.7±0.3 eV of excess translational energy at an electron energy of 61.3±0.3 eV. These results indicate that the sum of the excess electronic energy is -0.2±1.0 eV. Since the first excited state of either product (the ¹D state of C) is

1.27 eV above the ground state, it seems that both products are formed in their ground electronic states. These conclusions are summarized in Table II.

Nitric Oxide

The appearance potential of NO^+ was observed to be 9.28 ± 0.03 eV, in good agreement with previous observations (see Table III). Ionization to higher electronic levels of the ion was not observed in the limited range of electron energies (9 to 14 eV) investigated.

The negative ion O^- was observed to be formed by a resonance process with onset occurring at 5.0 ± 0.1 eV. It was not possible to determine the translational energy of the ion, but if it is assumed that the ion is formed with no excess translational energy, the ob-

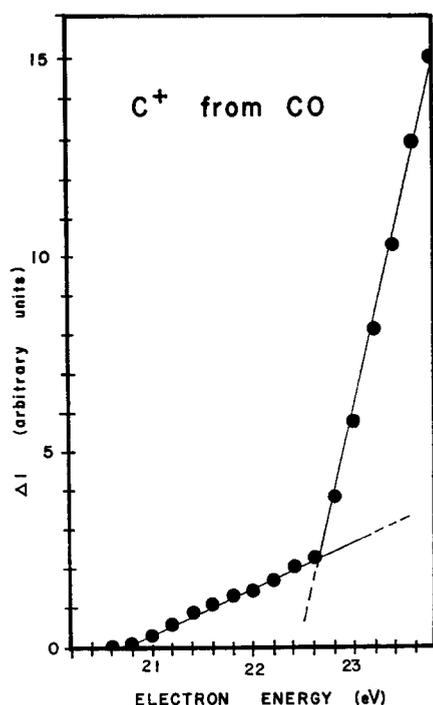


FIG. 4. Ionization efficiency curve for the production of C^+ from carbon monoxide.

served value agrees very well with the value of 5.01 eV calculated for Process 2, Table III.

The O^- ion is also formed by an ionic dissociation process, with onset occurring at 19.8 ± 0.1 eV. This agrees well with the value of 19.94 ± 0.14 eV determined for the appearance potential of N^+ , indicating that the two ions are probably formed simultaneously by an ion-pair process. Although it was not possible to determine the translational energy of the negative ion, the N^+ ion was observed to be formed with 0.32 ± 0.10 eV of translational energy at onset. The appearance potential for the ion-pair process, corrected for excess translational energy, is therefore 19.38 ± 0.32 eV. If both products are in their ground states, the calculated value is 19.55 eV [assuming $E.A.(\text{O}) = 1.48$ eV].²²

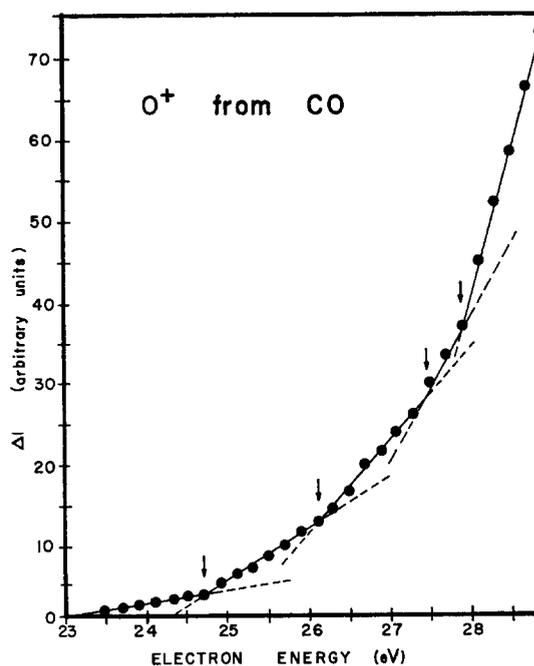


FIG. 5. Ionization efficiency curve for the production of O^+ from carbon monoxide.

As shown in Fig. 7 there is an increase in the efficiency of production of N^+ ions at 21.78 ± 0.11 eV. At this electron energy, the translational energy of the N^+ ions was observed to increase to 0.48 ± 0.10 eV. This value is interpreted as representing the translational energy of the N^+ ions formed by a new process occurring at electron energies greater than 21.78 eV. Consequently, the appearance potential corresponding to the formation of ions with no excess translational

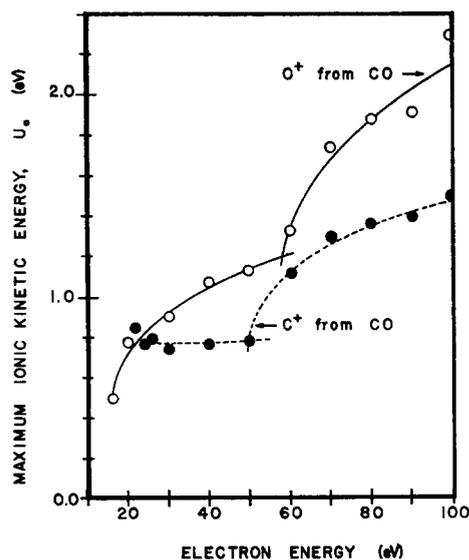


FIG. 6. Maximum excess translational energy vs electron energy for O^+ and for C^+ from carbon monoxide.

TABLE III. Ionic processes in NO.

Process	Products ^a	A.P. (eV)		
		This work	Previous studies	Spectroscopic
1	NO ⁺ (X ¹ Σ ⁺)	9.28±0.03	9.4 ^b	9.26 ^d
2	O ⁻ (² P)+N(⁴ S)	5.0±0.1	3.2 ^b	5.01 ^e
3	$\left\{ \begin{array}{l} \text{O}^-(^2P)+\text{N}^+(^3P) \\ \text{N}^+(^3P)+\text{O}^-(^2P) \end{array} \right\}$	19.3±0.3 19.38±0.3	19.8 ^b 19.9 ^b 20.0 ^e	19.55 ^e
4	N ⁺ (¹ D)+O(³ P)	20.88±0.29	21.7 ^b	21.03 ^e
5	$\left. \begin{array}{l} \text{N}^+(^1D)+\text{O}(^3P) \\ \text{or} \\ \text{N}^+(^3P)+\text{O}(^1D) \end{array} \right\}$	22.8±0.8	...	22.93 ^e 23.00 ^f
6	O ⁺ (⁴ S)+N(⁴ S)	19.96±0.40	18.9 ^b	20.10 ^e
7	O ⁺ (⁴ S)+N(² D)	22.4±0.4	...	22.48 ^e
8	$\left\{ \begin{array}{l} \text{N}^{2+}(^2P)+\text{O}(^3P) \\ \text{or} \\ \text{N}^{2+}(^3P)+\text{O}(^1D) \end{array} \right\}$	52.2±1.2	...	50.64 ^e 53.20 ^e
9	$\left\{ \begin{array}{l} \text{O}^{2+}(^3P)+\text{N}(^4S) \\ \text{or} \\ \text{O}^{2+}(^3P)+\text{N}(^2D) \end{array} \right\}$	56.4±1.2	...	55.25 ^e 57.63 ^e

^a The appearance potential refers to the first ion given, i.e., to the one on the left when two are formed.

^b Reference 13.

^c Reference 19.

^d Reference j of Table I.

^e Calculated assuming $D(\text{NO}) = 6.49$ eV [see H. D. Hagstrum, J. Chem. Phys. 23, 1178 (1955)] and $E.A.(\text{O}) = 1.48$ eV.²² Ionization potentials and electronic energy levels from Ref. 21.

energy is 20.88 ± 0.29 eV, which agrees well with the value of 21.03 eV for Process 4, Table III.

There is another break in the ionization efficiency curve for N⁺ at 23.3 ± 0.2 eV. Since there was no observed increase in peak width, it is assumed that the N⁺ ions arising from this new process are formed with less than 0.48 eV of translational energy. Since a lower limit for the translational energy cannot be set, the corrected value for this appearance potential must be in the range $23.2 (+0.4; -1.2)$ eV. This could be explained by either of the two processes listed in Table III.

The O⁺ ion was observed to be formed at 20.46 ± 0.10 eV, with 0.25 ± 0.15 eV of translational energy, thus indicating a corrected appearance potential, A.P.₀, of 19.96 ± 0.40 eV. This agrees well with the value of 20.10 eV calculated for the formation of the products in their ground states. A break in the ionization efficiency curve occurred at 22.59 ± 0.15 eV. Since there was no increase in peak width, it is assumed that the ions formed by this new process have less than 0.25 eV of translational energy. This indicates that the corrected appearance potential, A.P.₀, is in the range 22.0 to 22.9 eV. This probably corresponds to the formation of the N atom in its first excited state (Process 7, Table III).

As in the case of carbon monoxide, there is no indication of the simultaneous formation of N⁺ and O⁺ from

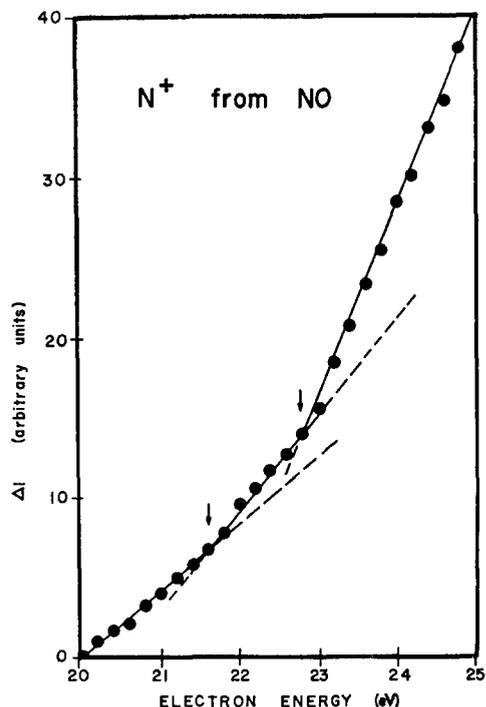


FIG. 7. Ionization efficiency curve for the production of N⁺ from nitric oxide.

an unstable NO^{2+} ion. A study of the translational energies of the fragments indicates that the O^+ and N^+ ions are formed with maximum translational energies of 7.5 and 5.7 eV, respectively. If these ions were produced by the decomposition of a doubly charged molecular ion, it would be expected that the lighter ion (N^+) would possess the greater amount of the excess translational energy.

The N^{2+} ion possessed 2.0 ± 0.5 eV of translational energy at its appearance potential, 56.0 ± 0.2 eV. These results indicate 1.6 ± 1.2 eV of excess electronic energy. Since the first excited state of the products is the 1D state of the oxygen atom, which lies 1.97 eV²¹ above the ground state, it is concluded that the products are those indicated in Table III, Process 8, although it must be admitted that this conclusion is somewhat tenuous.

The O^{2+} ion was formed with 2.5 ± 0.5 eV of translational energy at an electron energy of 61.62 ± 0.15 eV, thus indicating 1.1 ± 1.2 eV of excess electronic excitation. Since the first excited state of the products, the 2D state of N, is 2.38 eV above the ground state, it is not possible to identify the dissociation products from these data.

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Time-Correlation-Function Expressions for Linear and Nonlinear Transport Coefficients*

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Construction of a statistical-mechanical ensemble to represent a system known to be out of equilibrium is discussed. The consequences of the temperature, velocity, and chemical potential fields are formal time-correlation-function expressions for both linear- and higher-order transport coefficients. Many different forms of correlation functions are equivalent, which permits choice of the most useful for a given purpose. Onsager-type reciprocal relations appear to exist for only the linear coefficients.

I. INTRODUCTION

There is a rapidly increasing trend in statistical-mechanical studies of transport processes to adopt time-correlation-function representations of the transport coefficients as starting points. These formal representations are either accepted *a priori* or else are derived by any of a variety of methods.¹⁻⁹ An excellent review of these methods and of the uses of the correlation function has been given by Zwanzig.¹⁰

This paper treats the general formulation of non-equilibrium ensembles in a simple way in which the physical implications are apparent. This in itself may

prove useful to those who want to understand results based on the use of correlation functions or who want to use them themselves or extend similar theories to new domains. A major advantage of the approach is that it gives not just the linear consequences of gradients in local properties. Higher-order effects, such as non-Newtonian viscosity and normal stresses in viscous liquids, are easily formulated. From the form of the higher-order coefficients, it appears that Onsager-type reciprocal relations exist for only the linear coefficients. Stress is laid throughout the paper on the variety of formal starting points available and on the ease of passing from one equivalent form to another to obtain the best starting expression for the purpose at hand.

II. NOTATION¹¹

The N -particle distribution function f_N evolves according to the Liouville equation, which we write

$$i(df_N/dt) = i(\partial f_N/\partial t) - \mathcal{L}f_N = 0, \quad (1)$$

which defines the Liouville operator \mathcal{L} . Use of a Liouville formalism restricts the range of validity to

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