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MASS SPECTROMETRIC STUDY OF DISSOCIATIVE ATTACHMENT IN DIATOMIC MOLECULES
II. NO AND O_2

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ABSTRACT

The dissociative attachment (DA) processes of O^- ions in nitric oxide and oxygen are investigated using a 60° sector field mass spectrometer. In nitric oxide O^- appears at (7.43 ±0.2) eV and analysis of the DA curve indicates the probable existence of two other processes at 8.1 eV and 9.0 eV. In oxygen, only one process is observed at (3.45 ± 0.3) eV. For both molecules an attempt is made, using a Morse function, to establish the shape and the relative positions of the potential energy curves for the electronic states of the transient negative molecular species involved.

INTRODUCTION

The theoretical shape of the ionization efficiency curve of a dissociative attachment (DA) process obtained by electron impact has been discussed previously[1]. The kinetic energy distribution of the negative ion has been considered and a linear extrapolation method for the determination of the threshold values has been established. An attempt was made to deduce the relative position of the potential energy curve of the negative molecular ion decaying into a negative fragment ion and a neutral. This was applied to H^- appearing in hydrogen and O^- in carbon monoxide.

The purpose of this paper is to give the results obtained with the same technique in the case of the DA processes observed in nitric oxide and in oxygen.

I. EXPERIMENTAL

The instrument used and the way in which the ionization efficiency curves are recorded have been described previously[1].

II. RESULTS

A. DA process in NO

The only known DA process is the appearance of O^-. The ionization efficiency curve is shown in Fig. 1. The threshold of the DA process was found to be at (7.43 ± 0.2) eV. The maximum of the cross section is at (8.1 ± 0.2) eV. In order to calibrate the electron energy scale the appearance of S^- in CS_2 was used, the first threshold of which is at (3.02 ± 0.12) eV[9] with respect to O^- in carbon monoxide. This is in good agreement with previous results of Dorman[2] and Chantry[3].

Frost and McDowell[4] found a threshold at (6.99+0.05) eV, probably by means of the vanishing current method. The discrepancy with our result seems to be due to the method used for the determination of the threshold.

More recently, Hierl and Franklin[5] found a process at (5.0 ± 0.1) eV. In our experiments, no ion current was detectable below 6.5 eV.

On the high energy side of the main peak, the ionization efficiency curve shows a very long tail extending up to 11 eV, which is probably due to one or more successive DA processes. This was observed by some authors[2,3], whilst others do not mention it[4,5]. The total ionization efficiency curve published by Rapp and Briglia[6] shows the same structure as that observed by us, but with somewhat different intensities.

Fig. 1: *DA ionization efficiency curve of* O^- *in NO.*

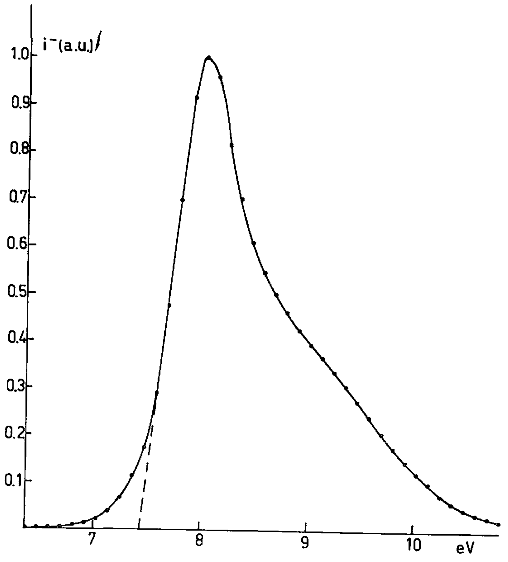
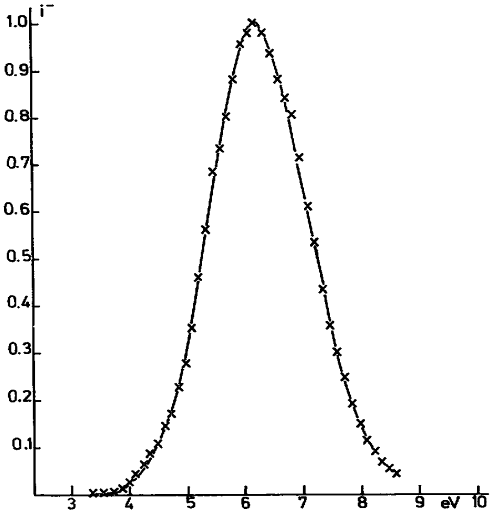


Fig. 2: *DA ionization efficiency curve of* O^- *in* O_2*.*



B. DA process in O_2

Only one DA process is observed in oxygen: the ionization efficiency curve is shown in Fig. 2. The position of the peak is characterized by three points (i) the vanishing current at (3.70 ± 0.3) eV, (ii) the linear extrapolation at (4.4 ± 0.2)eV and (iii) the maximum of the peak at 6.2 eV. The peak width at half-height is 2.0 eV.

The reference used to calibrate the electron energy scale was the process $O_2 + e^- \rightarrow O^-(^2P) + O^+(^4S) + e^-$ observed at 17.25 eV[7]. It is well known that the negative ion formed in this ion pair process appears without kinetic energy[8]. It has been verified[9] that the threshold of an ion pair process can be determined in the same way as for a DA process, using the first derivative of the ionization efficiency curve related to such processes[*].

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[*] This has recently been confirmed[9] by deconvolution of the first derivative of the ionization efficiency curves of ion-pair processes in diatomic and polyatomic molecules.

In Table 1, the results of previous work on the appearance of O^- in oxygen are given.

III. DISCUSSION.

A. Appearance of O^- in NO

(a) The process observed at 7.43 eV. Taking the values 6.487 eV[16] and 1.465 eV[17], respectively, for the dissociation energy of NO and the electron affinity of the oxygen atom, the threshold of the lowest energy process for the appearance of $O^-$by DA from nitric oxide

$$NO(X^2\Pi)+e^- \rightarrow N(^4S)+O^-(^2P)$$

should be at 5.02 eV. The energy difference of 2.31 eV, between the experimental and the calculated threshold energies, must be assigned to the kinetic energy (KE) and/or to the excitation energy of the fragments.

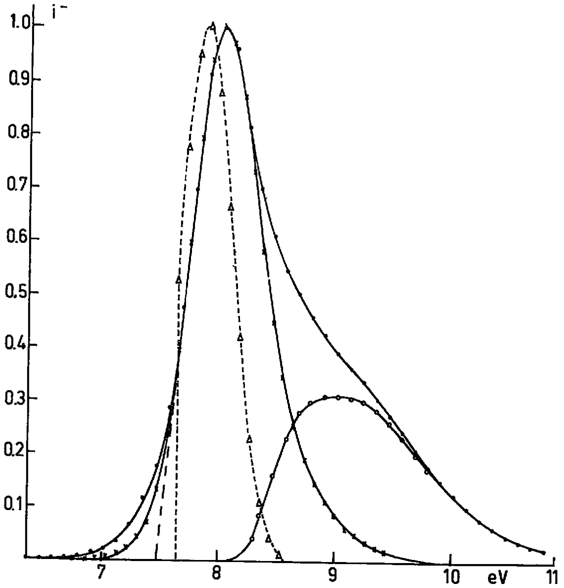
TABLE 1

Linear extr.	*Vanishing curve*	*Maximum*	*Ref.*
4.9			10[a]
	4.53	5.9	11[1,b]
4.7		6.5	12[c]
		6.7	8[c]
	4.4		13[1,c]
	3.75	6.2	14(?)
		6.0	2[a]
3.75		5.23	15[2,b]
4.4 ± 0.2	3.7 ± 0.3	6.2	this work[d]

(1) RPD. (2) Electron Energy Selector. Calibration: (a) O^-/CO at 9.3 eV; (b) SF_6^- at O eV; (c) electron retarding curve; (d) O^-/O_2 at 17.25 eV; (?) unknown.

Fig. 3 shows that the best agreement between the experimentally observed main peak shape of O^- in NO is given by an *f*(b) type convoluted model[1] with a total KE width of 1.0 eV.

***Fig. 3:** (•) Experimental ionization efficiency curve of O^- in NO; (x) convoluted model; (-$^\Delta$-) model; (o) curve obtained from the difference between the experimental curve and the convoluted model.*



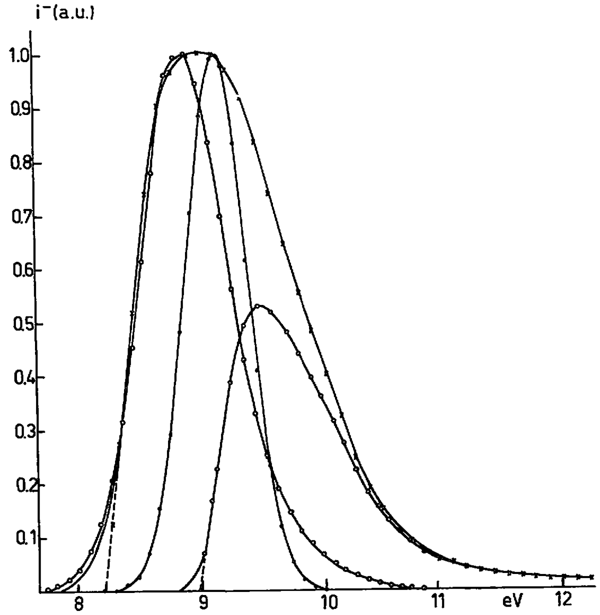
It follows that the negative ion appears at threshold without KE and this was recently confirmed by Chantry[3]. Therefore, the energy excess of 2.31 eV may correspond to electronic excitation energy of the nitrogen atom.

The first excited state of the nitrogen atom (^2D) lies 19,223 cm^{-1} (i.e. 2.38 eV)[18] above the ground state. It seems therefore that the process observed at 7.43 eV can be expressed by the following mechanism (calculated threshold: 7.40 eV)

$$\mathrm{NO}(X^2\Pi) + e^- \rightarrow \mathrm{NO}^{-}* \rightarrow \mathrm{N}(^2D) + \mathrm{O}^-(^2P) \qquad (1)$$

(b) Subtracting the properly convoluted curve for process (1) from the experimental peak, enables us to resolve the process which is responsible for the shoulder observed on the high-energy side of the main peak (Fig. 4). The threshold of this process is at (8.3 ± 0.2) eV.

Fig. 4: *(x) O^-/NO curve obtained by intensity difference; (o) convoluted model; (•) model; the peak at 9.0 eV (o) is obtained by difference. (See caption to Fig. 3.)*



Dorman[2] interprets this structure by a DA process in which the nitrogen atom appears in its second excited ^2P state at 28,840 cm^{-1} (i.e. 3.57 eV)[18] above the ground state. The energy difference between the ^2P and ^2D states is 1.19 eV.

The shape of the last peak corresponds to an *f*(c) model, where the whole $\Psi(E)^2$ is involved, i.e. the electronic transition is at or above the dissociation limit of a NO$^-$* electronic state.

We have shown[1] that in such cases the threshold value should be corrected by -0.25 eV: consequently the second process appears at (8.1 ± 0.2) eV.

It appears that the energy difference of about 0.7 eV between the two processes should be attributed to the KE carried away by the fragments. This interpretation is in agreement with the KE energy analysis made by Chantry[3]. We have shown[1] that the discrimination effects of the instrument used in our experiments has no detectable effect on the *shape* of the peak.

(c) *Fig. 4 shows the probable existence* of a third DA process producing O^- in NO. The threshold is at 9.2 eV. The energy difference between the first and the third process, 1.8 eV, does not correspond to an interval between two electronic states in the nitrogen atom. This energy excess is entirely converted to KE, in agreement with the KE analysis made by Chantry[3].

Only an *f*(c) model can account for this peak and the threshold must be corrected by -0.25 eV.

The symmetry of the peak, obtained by intensity difference (Fig. 5) can be explained by the shape of the potential energy curve involved in the electronic transition, as shown in Fig. 6.

***Fig. 5:** (O) O^- /NO (third peak): (x) convoluted model; (•) model.*

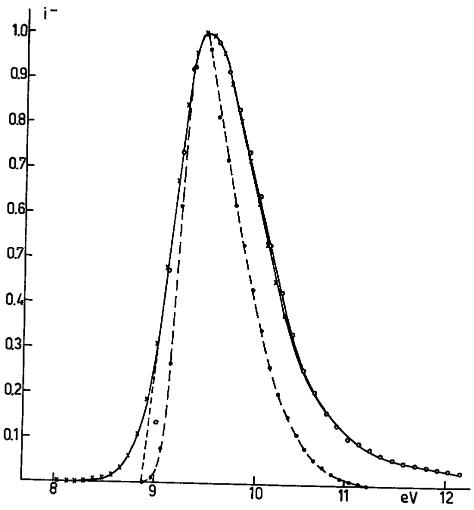
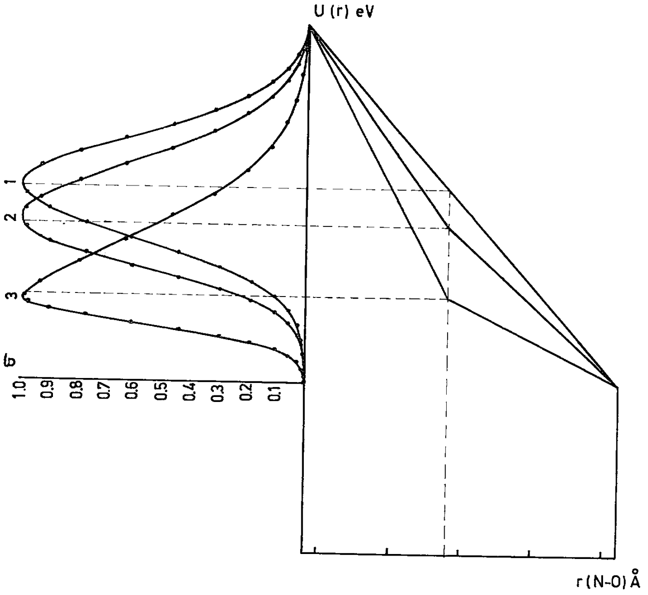


***Fig. 6:** Dependence of the form of the peak upon the shape of the potential energy curve concerned in the transition. The convolution of curve (3) takes account of the third process of O^-/NO.*



B. Appearance of O^- in O_2

Analysis of the ionization efficiency curves published by different authors indicates that the width at half-height of the DA peak of O^- in O_2 seems to be independent of the electron energy spread, when using either an electron energy selector, or the RPD technique, or a conventional electron beam. This has been confirmed by the convolution of an *f*(c) model having a total KE width over the range of 6.2 eV: the width at half-height is 2.0 eV. The resulting peak has a width at half-height of 2.05 eV (Fig. 7).

For such a spread, the contribution of the electron energy distribution is negligible and in this case the vanishing current method should give the true threshold for the process. In this case, O^- in oxygen appears at (3.7

± 0.3) eV, and taking a correction of -0.25 eV into account, at (3.45 ± 0.3) eV. The first appearance process of O^- in oxygen should be:

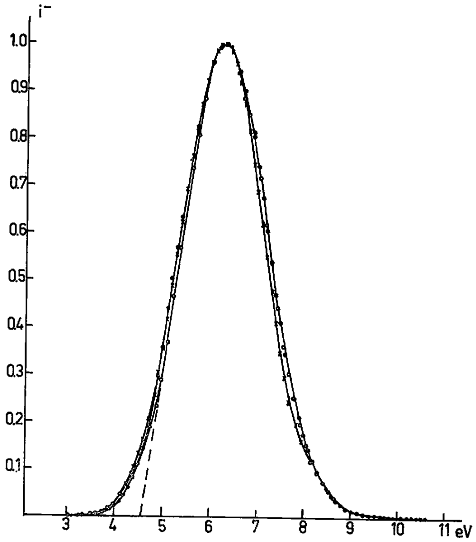
$$O_2(X^3\Sigma_g^-)+e^- \rightarrow O(^3P)+O^-(^2P)$$

Taking the values *EA*(O) = 1.465 eV[17] and D(O-O) = 5.080 eV[18] leads to a threshold of the DA process at 3.61 eV. Measurements made by Schulz[13] show that 0.5 eV KE are carried away by O^- at threshold; consequently the total KE involved in the process is about 1 eV at threshold.

If the process takes place through a transition to the repulsive part of an attractive potential energy curve relative to O_2^{-*}, the difference between the measured threshold and the KE involved in the process gives a dissociation limit at (2.45 ± 0.3) eV, which is (1.16 ± 0.3) eV lower than the calculated value.

The DA curve of O^- from O_2 was recorded at 526 °K. No vibrational excitation, at least only a rotational excitation of O_2 in the fundamental electronic state can be expected at this temperature, and will be of minor importance.

***Fig.7:** (•) Experimental ionization efficiency curve of O^- in O_2; (x) convoluted model: (o) model.*



It is well known[22] that the DA cross section is proportional to the "survival probability"[*], which is a function of the electron energy. This factor causes a shift of the DA threshold to lower energies. Such an effect has been previously observed[1] in H from H_2. A quantitative evaluation of the shift due to this factor together with that from the temperature of the gas, has been attempted by O'Malley[19] for the DA of O^- from O_2. At room temperature the shift has been evaluated to be approximately 0.8 eV.

IV. DRAWING OF POTENTIAL ENERGY CURVES

A. DA processes in nitric oxide

As shown above, analysis of the DA peak indicates the possible existence of three processes. We have shown that the ground state of NO^- is not involved in the first process. Gilmore[20] described the $X^3\Sigma^-$ state by the electronic configuration.

$$KK\ldots(5\sigma)^2(1\pi)^4(2\pi)^2(6\bar{\sigma})\ X^3\Sigma^-$$

This state as well as three repulsive states $^3\Pi$, $^5\Pi$ and $^5\Sigma^-$ have been drawn in Fig. 8 (dotted curves).

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[*] This is the probability that the negative molecular ion does not decay through autodetachment before dissociating into a negative fragment ion and a neutral.

(a) The process responsible for the dissociative attachment

$$NO(X^2\Pi) + e^- \rightarrow O^-(^2P)+N(^2D) \qquad (1)$$

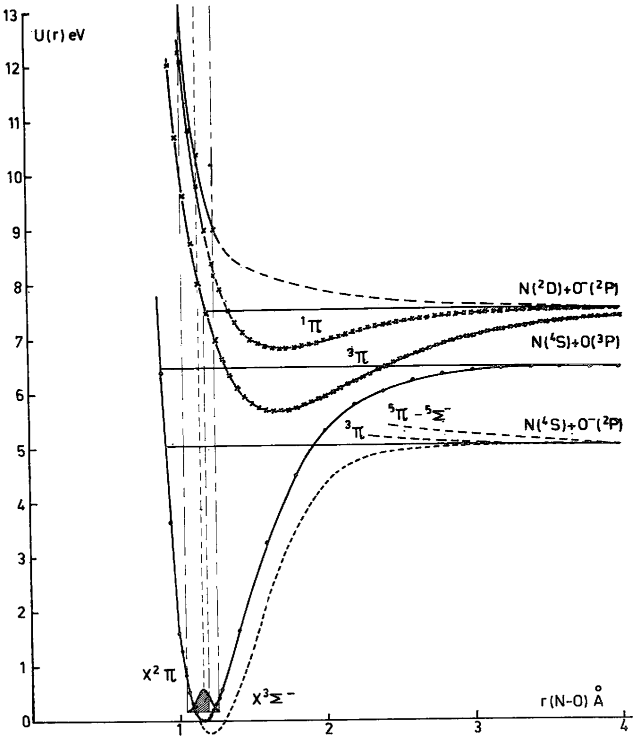
occurs through a transition to a dissociation limit at 7.40 eV of an excited state of the molecular ion $NO^{-}*$. The parameters of the Morse function needed to draw the curve shown in Fig. 8 are:

$$\beta = 1.45 \times 10^8 \text{ cm}^{-1};\ r_e = 1.67 \times 10^{-8} \text{ cm};\ D_e = 1.86 \text{ eV}$$

The excitation of a 2π electron, centered on nitrogen[21] to a 6σ orbital leads to singlet and triplet Π states. Probably the $^3\Pi$ state would be the most stable, the $^3\Pi$ state electron configuration is

$$KK \ldots (5\sigma)^2(1\pi)^4(2\pi)(6\sigma)\ ^3\Pi$$

Fig. 8: *Potential energy curve relative to NO and NO⁻ involved in the process observed (x).*



(b) Mechanism (1) is responsible for the threshold at 8.1 eV, the negative ion carrying away 0.4 eV kinetic energy. The DA process should occur through a transition to the repulsive part of a potential energy curve having a dissociation limit at 7.40 eV.

In this case, a system of four linear equations, giving the four parameters x, β, r_e and D_e, could only be resolved by a method of successive approximation. The calculations were performed on an IBM 7040 computer.

Fig. 8 shows the potential energy curve defined by the parameters.

$$\beta = 2.04 \times 10^8 \text{ cm}^{-1};\ r_e = 1.69 \times 10^{-8} \text{ cm};\ D_e = 0.73 \text{ eV}$$

The negative molecular ion, above the $^3\Pi$ state, can be described by the MO configuration

$$KK \ldots (5\sigma)^2(1\pi)^4(2\pi)(6\sigma)\ ^1\Pi$$

and is in a singlet Π state.

(c) The O^- ions appearing at 9.0 eV are endowed with a large amount of KE. The upper electronic state concerned in this transition should be repulsive, the dissociation limit being at 7.40 eV. The curve shown in Fig. 8 has been drawn taking into account the symmetry of the peak obtained by intensity difference (see Fig. 6).

B. DA process in oxygen

In a previous section, we reported that in oxygen, the DA process, due to the mechanism:

$$O_2(X^3\Sigma_g^-)+e^- \rightarrow O(^3P)+O^-(^2P)$$

occurs with a KE energy distribution spread over 6.2 eV.

The potential energy curve representing the fundamental state $X^2\Pi_g$ described by the MO configuration

$$\mathrm{KK}\ldots(5\sigma)^2(1\pi)^4(2\pi)^3\ X^2\Pi_g$$

has been drawn by Gilmore[20] and is reproduced in Fig. 9.

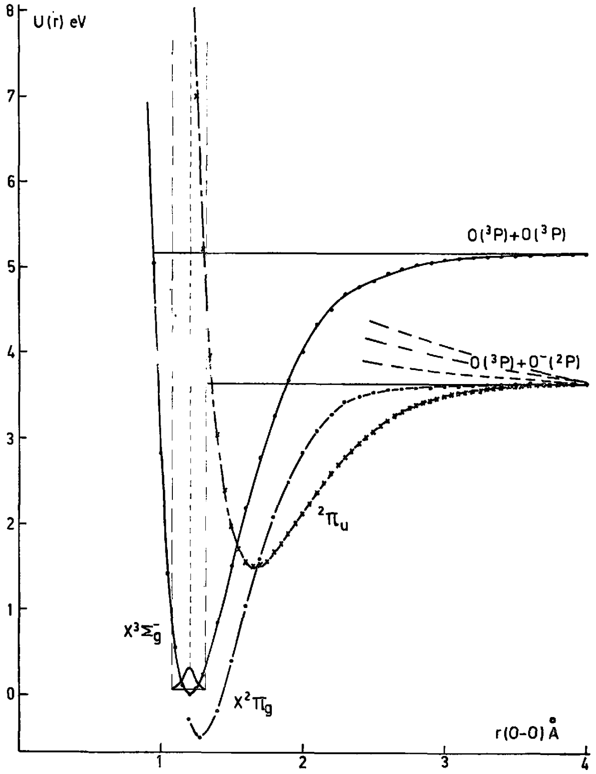
The data obtained by electron impact lead to the conclusion that the part of the potential energy curve concerned in the transition and giving rise to O^- by DA, belongs to an excited state of O_2^- with the dissociation limit at 3.6 eV. We tried to calculate this potential energy curve by a method of successive approximation which provides a large set of values for the four parameters x, β, r_e and D_e. One curve has been drawn in Fig. 9 with the following parameters:

$$\beta = 2.29\times10^8\ \mathrm{cm}^{-1};\ r_e = 1.67\times10^{-8}\ \mathrm{cm};\ D_e = 2.14\ \mathrm{eV}$$

The electronic state concerned should be the $^2\Pi_u$ state[20] described by

$$\mathrm{KK}\ldots(5\sigma)^2(1\pi)^3(2\pi)^4\ ^2\Pi_u$$

Fig. 9. *Potential energy curve relative to O_2 and O_2^- involved in the process observed (x).*



O'Malley[19] calculated the corresponding potential energy curve: the dissociation energy and equilibrium internuclear distance were found to be (1.0 + 0.5) eV and about 1.70 Å respectively.

CONCLUSIONS

With the help of the results of previous work and by detailed examination of the DA processes observed in nitric oxide and oxygen, it has been possible, in the case of the DA process observed in NO, to assert the possible existence of three processes. A qualitative interpretation of these results in terms of potential energy curves is attempted.

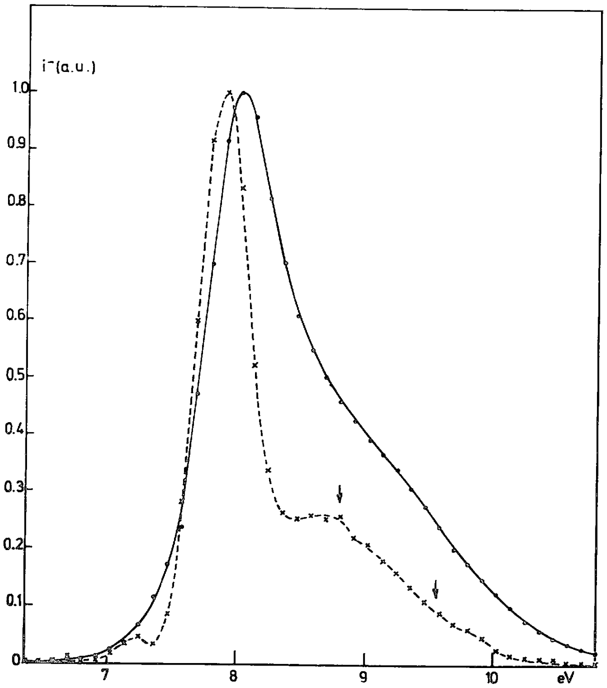
In the case of the DA process in oxygen, it was found that the "vanishing current" method gives the real threshold. This is due to the large KE spread which is negligible with respect to the electron energy distribution used in our experiments. The threshold determined in this way has been interpreted in the frame of the DA theory proposed by O'Malley.

APPENDIX

The results obtained in this paper by the convolution technique have recently been confirmed in this laboratory by means of a deconvolution method of McNeil and Thynne[23], who used a technique of successive approximation instead of that proposed by Morrison[24] based on Fourier transforms.

This technique has been applied to the DA processes and to the particular case of O^- from NO. The result is shown in Fig. 10. The maximum of the peak is shifted to lower energies by 0.1 eV and the width at half-height is 0.5 eV, in excellent agreement with the model that we proposed for convolution. The fine structure previously resolved (Section IIIA, b and c) appears by deconvolution. The arrows in Fig. 10 show the positions of the maxima as defined by the convolution technique.

Fig. 10: *DA curve of O^- from NO. (•) Experimental curve; (x) deconvoluted curve.*



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REFERENCES

1 R. LOCHT AND J. MOMIGNY, *Int. J. Mass Spectrom. Ion Phys., 2* (1969) 425.

2 F. H. DORMAN, *J. Chem. Phys.,* 44 (1968) 3856.

3 P. J. CHANTRY, *Phys. Rev., 172* (1968) 125.

4 D. C. FROST AND C. A. MCDOWELL, *J. Chem. Phys.,* 29 (1958) 1424.

5 P. M. HIERL AND J. L. FRANKLIN, *J. Chem. Phys.,* 47 (1967) 3154.

6 D. RAPP AND D. D. BRIGLIA, *J. Chem. Phys.,* 43 (1965) 1480.

7 V. H. DIBELER AND J. A. WALKER, *J. Opt. Soc. Am.,* 57 (1967) 1007.

8 P. J. CHANTRY AND G. J. SCHULZ, *Phys. Rev.,* 156 (1967) 134.

9 R. LOCHT, unpublished work.

10 J. MARIOTT AND J. D. CRAGGS, *Applied Mass Spectrometry,* Inst. of Petroleum, London, 1956, p.173.

11 D. C. FROST AND C. A. MCDOWELL, *J. Am. Chem. Soc,* 80 (1958) 6183.

12 J. D. CRAGGS, R. THORBURN ABD B. A. TOZER, *Proc. Phys. Soc.,* 240A (1957) 473.

13 G. J. SCHULZ, *Phys. Rev.,* 128 (1962) 178.

14 P. L. RANDOLPH AND R. GEBALLE, *Thesis,* University of Washington, 1958.

15 C E. BRION AND G. E. THOMAS, *Int. J. Mass Spectrom. Ion Phys.,* 1 (1968) 25.

16 G. HERZBERG, *Spectra of Diatomic Molecules,* Van Nostrand, New York, 1950.

17 S. J. SMITH AND L. M. BRANSCOMB, *J. Res. Natl. Bur. Std.,* 55 (1955) 165.

18 C. E. MOORE, *Atomic Energy Levels,* Vol. 1, *Natl. Bur. Std. (U.S.), Circ.,* 467 (1949).

19 T. F. O'MALLEY, *Phys. Rev.,* 155 (1967) 59.

20 F. R. GILMORE, *J. Quant. Spectrosc. Radiat. Transfer,* 5 (1969) 369.

21 H. LEFEBVRE-BRION AND C. M. MOSER, *J. Chem. Phys.,* 44 (1966) 2951.

22 T. F. O'MALLEY, *Phys. Rev.,* 150 (1966) 14.

23 K. A. G. MCNEIL AND J. C. J. THYNNE, *Int. J. Mass Spectrom. Ion Phys.,* 3 (1969) 35.

24 J. D. MORRISON, *J. Chem. Phys.,* 39 (1963) 200.