

MASS SPECTROMETRIC STUDY OF ION-PAIR PROCESSES IN DIATOMIC MOLECULES: H₂, CO, NO AND O₂

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ABSTRACT

The appearance of ion-pair processes has been studied in H₂, CO, NO and O₂. The different thresholds successively observed for each process have been interpreted. Using the results from the convolution of theoretical models of the ionization efficiency curves and the deconvolution of their first differential, it was possible: (i) to propose a method for the determination of the threshold energy of an ion-pair process, (ii) to show that, except for H₂, the shape of the cross-section of an ion-pair process as a function of the electron excess energy is a step-function and (iii) to determine the kinetic energy distribution of the negative ions and consequently to form an idea about the relative position of the potential energy curves of the excited states of the molecule, decaying by ion-pair process, with respect to the ground state of the molecule. Our analysis suggests that, for CO and NO, some of the observed absorption bands, labelled by Tanaka as P_i ($i = 1-5$), might be related to the existence of some excited states of these molecules, correlated with an ion-pair as dissociation products.

INTRODUCTION

A detailed examination of the shape of the dissociative electron attachment (DA) peaks, as observed in H₂, CO, NO and O₂^{1,2} by electron impact, has led us through an interpretation of the DA peak's theoretical shape and of the negative ion kinetic energy distribution, to a non-arbitrary method for the determination of the threshold energy of a DA process and has enabled us to form a rough estimate of the relative position of the potential energy curves, as expressed in the Morse approximation, of the temporary negative molecular ions AB⁻.

In this paper we want to study the ion-pair processes as they are induced by electron impact in the same molecules.

These processes, of relatively low intensity, if they are considered at high electron (or photon) energies, are of leading importance, however, to interpret the appearance of positive fragment ions, as it results from some papers published by Dibeler^{3,4}, Momigny⁵ and Dorman and Morrison^{6,7}.

The following problems will be successively considered: (1) an attempt to propose a mechanism for the appearance of ion-pairs, (2) a discussion about the shape of the function which expresses the cross-section dependence of such processes upon the electron energy excess, and (3) the justification of a method to be used for the determination of threshold energies.

1. EXPERIMENTAL

The instrument and the experimental conditions used for the ionization efficiency curves recording, have been described elsewhere^{1,2}. An electronic trap current of 20 μ A, instead of 10 μ A in the previous works, is used in order to improve the measured intensity of the negative ions. The linearity of the electron energy scale was not affected by such an increase; this has been verified in each case by recording a portion of the ion-pair efficiency curve at 10 μ A. No energy shift was observed.

The references used for the electron energy scale calibration are the DA processes observed in H₂, CO and NO, at (13.78 \pm 0.08) eV, 9.6 eV and (7.43 \pm 0.2) eV, respectively^{1,2}. In the case of O₂, no calibration gas should be used, the electron energy scale for the DA process in oxygen² being calibrated by the first threshold of the ion-pair process occurring at (17.25 \pm 0.01)eV, as determined by photo-ionization^{4,8}.

In order to improve the data, the first differential of the ionization efficiency curves, as well as the convolution of theoretical models of these curves and their deconvolution, have been used. The first differential ionization efficiency curves given in the following sections are the average of ten independent measurements.

(a) *The first differential of ion-pair efficiency curves*

The first differential with respect to the electron energy of the ion-pair efficiency curves was obtained by the method proposed by Cantone⁹ and his colleagues, analytically expressed by:

$$\left[\frac{\Delta I_{\text{ion}}}{\Delta E} \right]_{E_N} = \frac{J_{N+2} - J_{N-2}}{E_{N+2} - E_{N-2}}$$

Where

$$J_N = \sum_{k=n-2}^{n+2} (I_{\text{ion}})_k$$

In order to use this technique, a Fortran IV program has been written by Leclerc¹⁰; the calculations were performed on the IBM 7040 computer.

(b) *The convolution of theoretical models and the deconvolution of experimental data*

The convolution of theoretical models of the ionization efficiency curves was used in the same way as described previously^{1,2}.

The use of the deconvolution of the ionization efficiency curves based on Fourier transforms^{11,12} is limited by the height of the noise level on experimental recordings. Recently an iterative method including noise smoothing has been successfully used by MacNeil and Thynne¹³. A Fortran IV program has been written in this laboratory by Leclerc¹⁴ and the calculations were performed with the IBM 7040 and the 360/44-65 computers. The latter has been applied to direct ionization efficiency curves and also to their averaged first derivative.

2. EXPERIMENTAL RESULTS

(a) *In H₂ only one process is observed.* The direct ion-pair efficiency curve and its first derivative are shown in Figs, 1a and 1b. Both the deconvoluted direct curve and its first differential show a sharp onset at (17.28 ± 0.16) eV. The maximum of the first derivative lies at 18.0 eV and its width at half-height is 0.90 eV.

(b) *In carbon monoxide,* the situation is given in Figs. 2a and 2b. Seven processes are observed in the first derivative of the ion-pair efficiency curve from O⁺ in CO. The previous results and those obtained in this work are collected in Tables 1a and 1b, respectively.

TABLE 1a : THRESHOLD ENERGIES OF IP PROCESSES OF O⁺ FROM CO, NO AND O₂ (PREVIOUS WORKS)

	Ref. 6	Ref. 8	Ref. 15	Ref. 16, 17	Ref. 18	Ref. 19	Ref. 20
O ⁺ /CO	21.0 ± 0.1	-	20.9 ± 0.2	20.9 ± 0.2	-	-	-
O ⁺ /NO	-	-	19.8 ± 0.2	19.8 ± 0.2	19.8 ± 0.2	19.55 ± 0.04	
O ⁺ /O ₂	17.2 ± 0.1	17.26 ± 0.02	18.9 ± 0.4	17.1 ± 0.2	-	-	17.3
	19.7 ± 0.1			20.2 ± 0.2			18.3
	20.4 ± 0.1						21.22 ± 0.05

The maximum of the first peak is at (21.6 ± 0.05) eV and its width at half-height is 0.92 eV. The deconvolution enables us to resolve completely the threshold of a process starting at 22.45 eV.

Fig. 1a. Direct IP ionization efficiency curve of H in H₂: (●) direct curve, (x) deconvoluted curve.

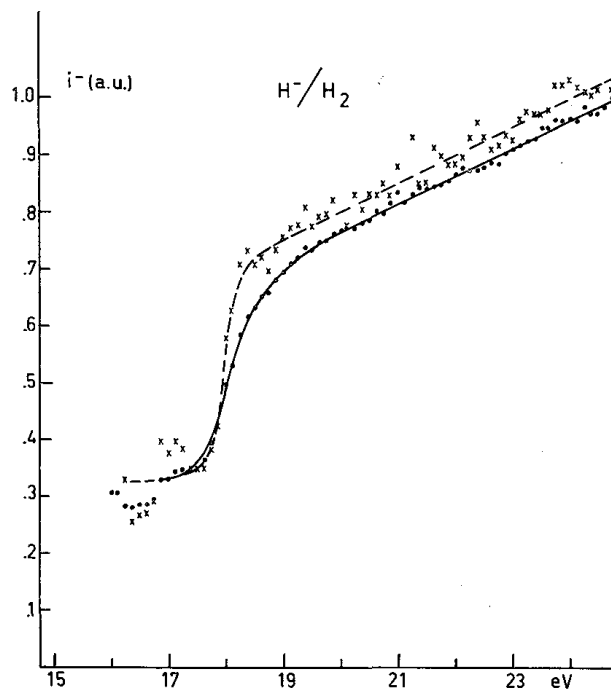


Fig. 1b. First derivative of the IP ionization curve of H in H₂: (●) undeconvoluted, (x) de-convoluted. The error bars gives the largest deviation from the arithmetic mean on each point.

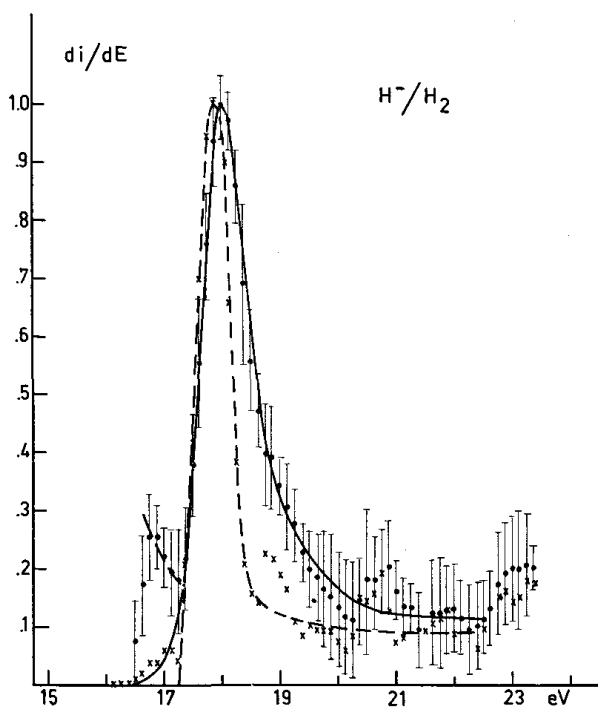
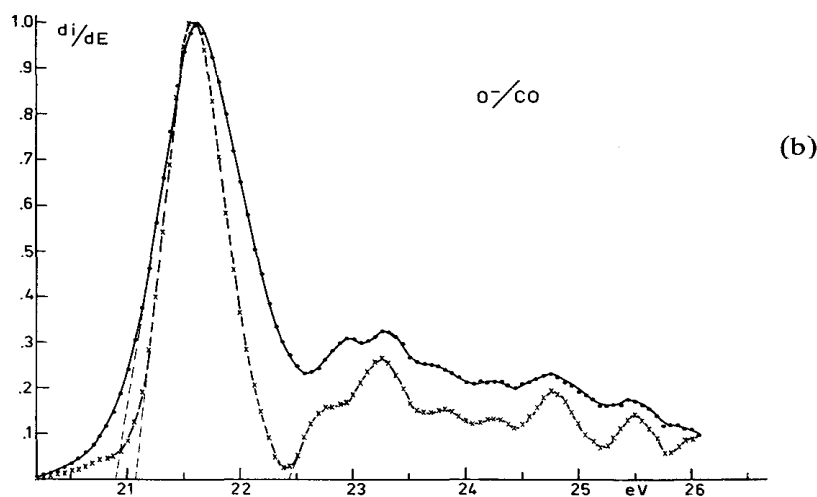
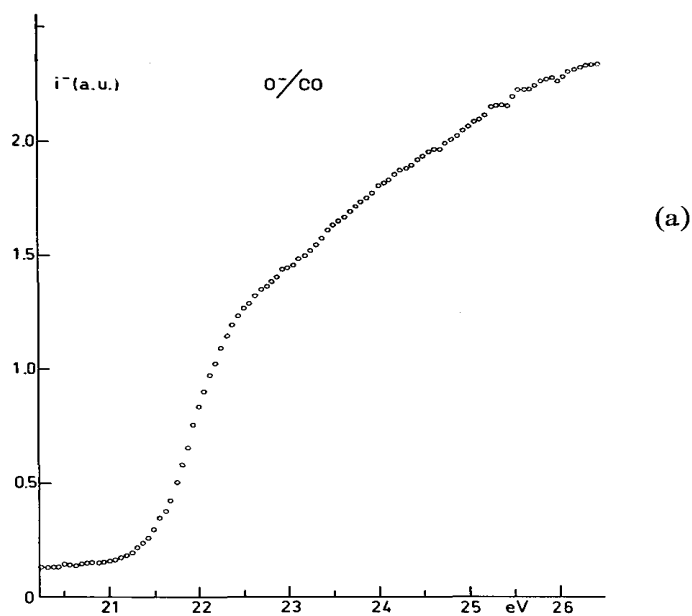
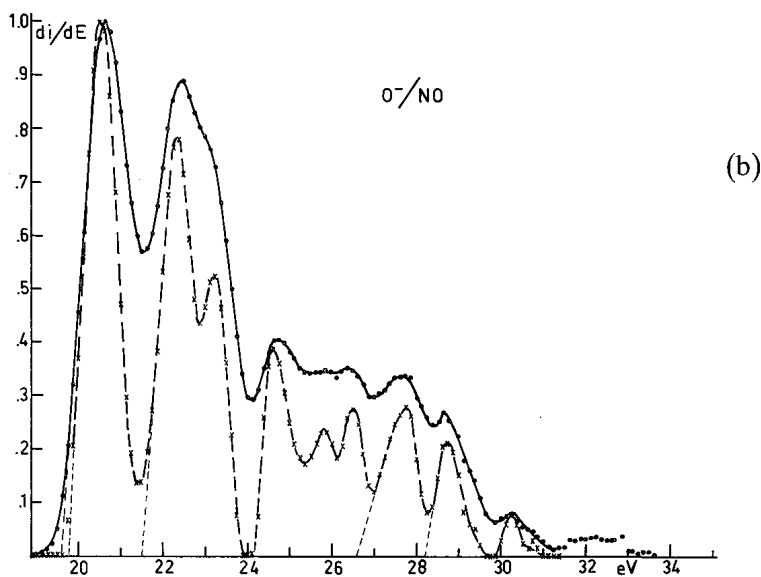
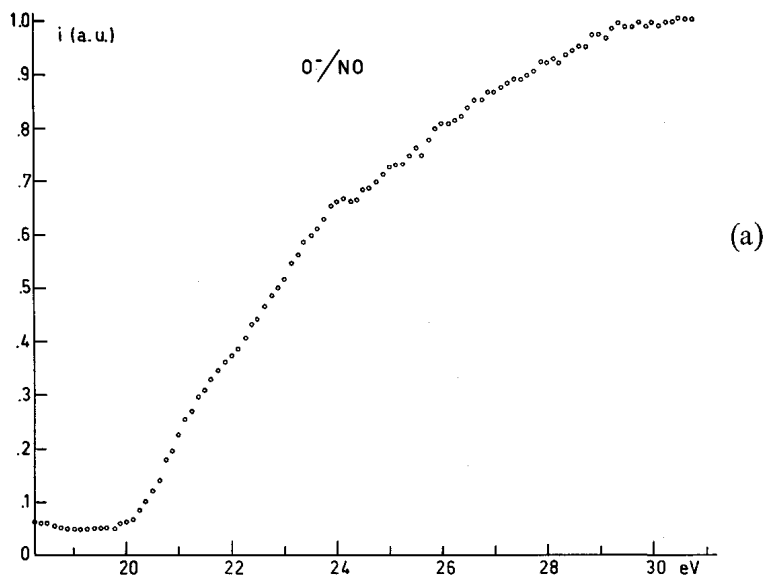


Fig. 2. (a) Direct IP ionization efficiency curve of O^- in CO. (b) First derivative of the IP ionization curve of O^- in CO: (●) experimental, (x) deconvoluted.



(c) The ion-pair processes observed for O^- in NO are shown in the first derivative of the O^- ionization efficiency curve (Figs. 3a and 3b). Both the previous results and those obtained in this work are collected in Tables 1a and 1b.

Fig. 3. (a) Direct IP ionization efficiency curve of O^- in NO. (b) First derivative of the IP ionization curve of O^- in NO: (••) experimental, (x) deconvoluted.



The maximum of the first peak occurs at (20.6 ± 0.2) eV.

(d) For O^- appearing in O_2 by ion-pair process, the situation is given in Figs. 4a and 4b (direct ionization efficiency curve and its first differential). Both the previous results and the present ones are collected in Tables 1a and 1b.

Fig. 4. (a) Direct IP ionization efficiency curve of O^- in O_2 . (b) First derivative of the IP ionization curve of O^- in O_2 : (•) experimental, (x) deconvoluted.

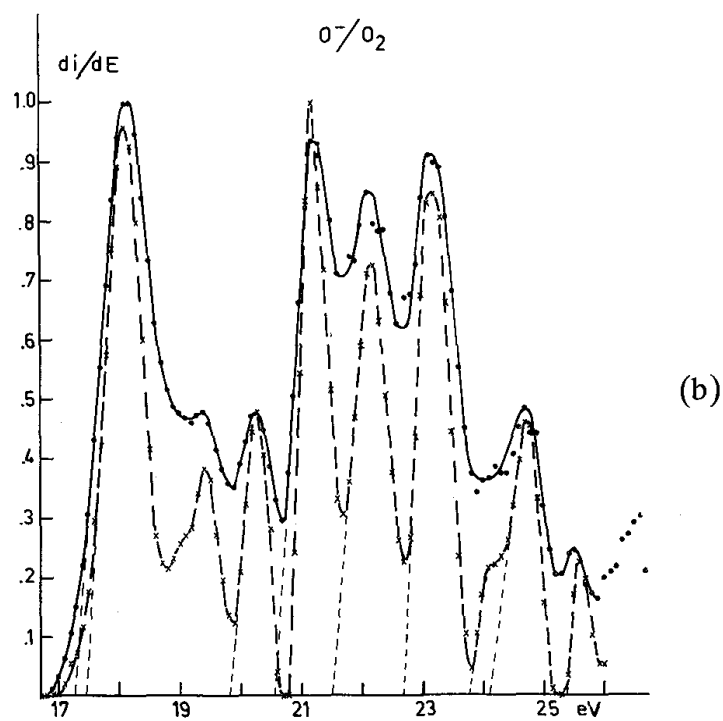
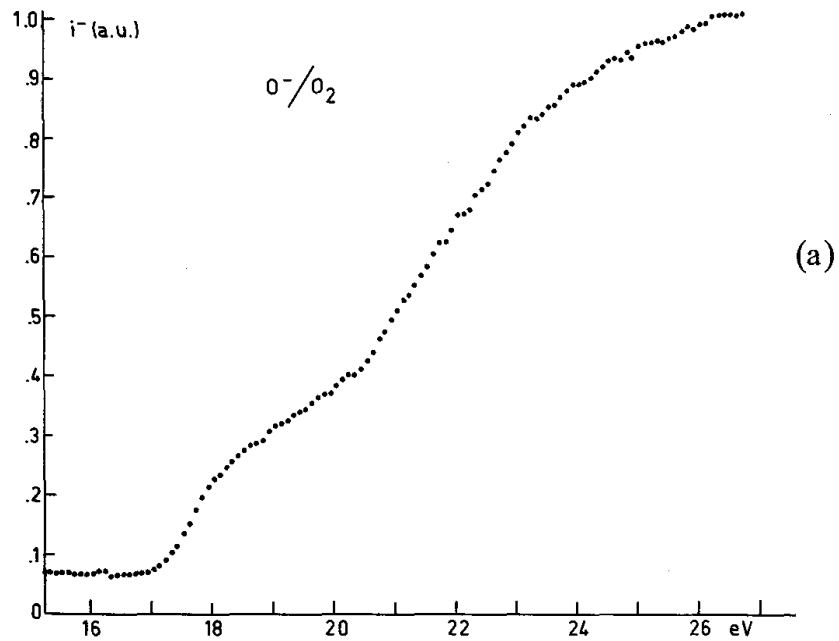


TABLE Ib THRESHOLD ENERGIES OF IP PROCESSES OF O FROM CO, NO AND O₂ (this work)

O/CO		O/NO		O/O ₂	
Ist Diff.	Deconv.	Ist Diff.	Deconv.	Ist Diff.	Deconv.
20.88 ± 0.02		19.6 ± 0.2		(17.25 ± 0.2)	
—	{22.45	—	{21.4	—	18.9*
22.95 ± 0.1*	{22.80*	22.5 ± 0.2*	{22.2*	19.4 ± 0.3	19.2*
23.25 ± 0.1*	23.10*	~23*	23.1*	—	{19.6
23.70 ± 0.3*	23.65*	—	{24.0	20.3 ± 0.2*	{20.0*
24.30 ± 0.2*	24.10*	24.7 ± 0.3*	{24.5*	20.5 ± 0.1	{20.6
24.75 ± 0.1*	24.60*	—	25.7*	21.2 ± 0.1*	{21.0*
25.45 ± 0.2*	25.30*	—	{25.5	—	{21.3
		26.4 ± 0.3*	{26.4*	22.1 ± 0.2*	{21.95*
		—	{26.4	—	{22.50
		27.7 ± 0.2*	{27.6*	23.2 ± 0.2*	{22.95*
		—	{28.0	—	{23.55
		28.6 ± 0.2*	{28.6*	—	{24.00*
		—	{29.7	—	{23.90
		30.2 ± 0.2*	{30.1*	24.7 ± 0.3*	{24.75*
				—	{25.20
				25.5 ± 0.3*	{25.40*

Ist Diff. = first differential of direct IP efficiency curves. Deconv. = deconvoluted first differential curves.

* Position of the maximum of the peak.

3. DISCUSSION

A. Preliminary considerations about the ion-pair process

Before the examination of different cases reported above, the following topics need to be discussed.

(a) *The shape of the ionization efficiency curve of ion-pair processes* The experimentally observed shape of the ionization efficiency curve of the ion-pair formation cross section $\sigma(E)$, where E is the energy of the incident particle, will be, in general, conditioned by three factors: (1) the electronic transition probability function between the ground state of the molecule and the excited state which is decaying by ion-pair process, (2) the threshold law and (3) the occurrence, in the instrument used, of a non-monoenergetic electron beam and of a discrimination against those ions which are carrying kinetic energy.

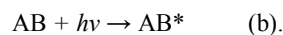
The first condition is realized if the complete efficiency of the deconvolution process used is assumed. We have shown¹ that the second assumption is fulfilled for the instrument used in our experiments.

As far as only one excited state is concerned in the electronic transition which gives rise to the ion-pair formation, the ionization efficiency curves as obtained by electron impact, are sigmoidal curves (Fig. 1a): by photoionization, peaks are observed^{3,4,8}.

The occurrence of a sigmoidally shaped curve by electron impact and of a peak by photon impact, is characteristic of excitation processes, such as:

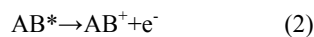


or



For the photon impact, the process of eqn. (1b) is a resonant one; for the electron impact, the excitation probability of the molecule, according to eqn. (1a), is a function $\Phi(E - E_T)$ of the excess energy of the impinging electron with respect to the threshold energy E_T of the process under consideration.

In a second step, the excited species AB^* may follow two different reaction paths



i.e. autoionization or dissociation into an ion-pair. If we recall that the Franck-Condon transition to AB^* takes place in some 10^{-16} sec the decay of AB^* through process (3) takes place in a time of the order of one vibration, i.e. 10^{-13} sec. During this time the products of reaction (1a) are very distant from one another. Consequently, the ionization efficiency curve for the ion-pair formation reflects principally the excitation probability function of the molecule.

The shape of the excess energy function $\Phi(E-E_T)$ has been discussed by Dorman et al.⁶ These authors propose a step-function, the first derivative of which is a δ function. We will see, in the next sections, that this is confirmed in most of the cases studied in this work; it is not, however, in the case of H^+ appearing in H_2 .

For reasons of easiness, we will base our discussion on the deconvoluted first differential of the ion-pair efficiency curves. It seems to be reasonable to assume that the deconvoluted first derivative of the ion-pair efficiency curve will be shaped as the ionization efficiency curve obtained from photon impact experiments. The resolution obtained by the deconvolution method is essentially limited by the smallest electron energy step which results in a measurable ion current variation in the ionization curve recordings.

The first differential of the ionization efficiency curve of ion-pair formation, as obtained by electron impact, is a peak of finite width (Figs, 1b to 4b).

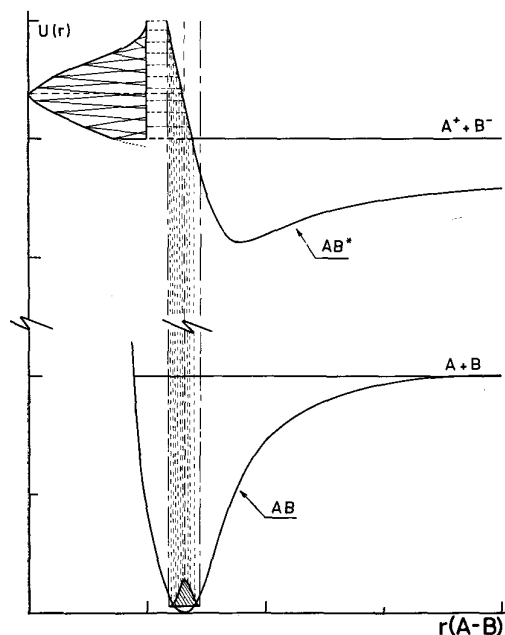
If we assume that, at the temperature of the ion source, the only ground vibronic state of AB is populated, the dissociation of the molecule into an ion-pair is only allowed by a transition from the ground state up to the continuum of the excited state AB^* . The transition probability function is given, in this particular case, by the square of the wave function associated with the ground vibronic state of the molecule. As in the interpretation of continuous spectra²³, the shape of the continuum is given, in a first approximation, by the reflexion of $|\Psi|^2$ in that part of the potential energy curve of AB^* which leads to A^+ and B^- .

The deconvoluted first differential of the ion-pair efficiency curve must be the envelope of successive δ functions corresponding to the transition probability at each internuclear distance, as schematically shown in Fig. 5.

Consequently, the peak shape depends upon: (i) the relative position of the potential energy curves of the AB and AB^* states and (ii) the shape of the repulsive part of the potential energy curve of the AB^* state in the Franck-Condon region. These two factors determine the kinetic energy distribution of both the negative and positive ions, as it has been pointed out for the peak shape of dissociative attachment processes in diatomic molecules¹.

Finally, we notice that by photoionization experiments, using mass analysis (refs. 4, 7, 8), the width at half height of the peak is narrower as observed by electron impact. A strong kinetic energy discrimination, occurring in the mass spectrometer used for the photoionization experiments, might be responsible for the peak-width discrepancy, especially if the focussing conditions are chosen so as to maximize the molecular ion-beam intensity. It should be recalled here that in our experiments these conditions were adjusted in order to maximize the O^- dissociative attachment peak from CO , where the O^- ions are known to carry away 0.3 eV kinetic energy¹.

Fig. 5. Potential energy curve diagram for a diatomic molecule: AB is relative to the ground electronic state, AB^* is relative to an ionic state. The Franck-Condon region is limited by dotted lines.



(b) *The determination of the threshold energy of ion-pair processes*

From the previous discussion it is possible to propose a non-arbitrary method for the determination of the threshold of an ion-pair process.

In previous works, devoted to the appearance of ion-pair processes, the threshold was arbitrarily taken at the maximum of the peak of the first derivative⁶ or by the "vanishing current" method of the direct curve^{15,16,19,20}. It has been shown²¹ that the latter often gives a too low value for the threshold. As it has been pointed out in Section 3A(a) the former method is generally erroneous: the maximum corresponds to the maximum of the transition probability. This method should give a correct threshold only in the case where the electronic transition takes place at the dissociation limit of an excited state AB^* which rises above the asymptote at, or lower than, the equilibrium internuclear distance of the ground state AB .

As in the case of DA processes, the intercept of the linear extrapolation of the left-hand side of the peak in the first derivative efficiency curve with the electron energy axis, will give at best the threshold energy of an ion-pair process. This is justified by the preceding discussion.

In this case also a correction of the same order of magnitude, i.e. of - 0.25 eV, as in DA processes^{1,2}, has to be made when the peak shape of the reference and of the ion to be measured are different, i.e. when an $f(c)$ -type peak has to be compared with an $f(a)$ - or an $f(b)$ -type curve (see refs. 1 and 2).

B. The H ion in H₂

The only previous work mentioning an ion-pair process in H_2 is from Kvostenko and Dukel'skii²². Figs. 1a and 2b show a sharp rise of the negative ion current at the threshold. We have tried to fit a convoluted model to the first differential peak. Within the estimated error on the experimental points, two models are possible (Figs. 6a and 6b). In both cases, the H^- ion appears without kinetic energy. The threshold of (17.28 ± 0.16) eV is in good agreement with the a priori calculated onset of 17.31 eV, taking $D(H_2) = 4.47$ eV²³, $IP(H) = 13.59$ eV²⁴ and $EA(H) = 0.75$ eV²⁵. No correction of energy has to be made, the reference ion appearing without KE¹.

The most probable interpretation of this ion-pair process is:

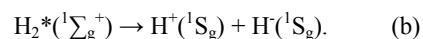
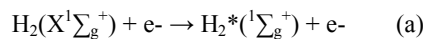
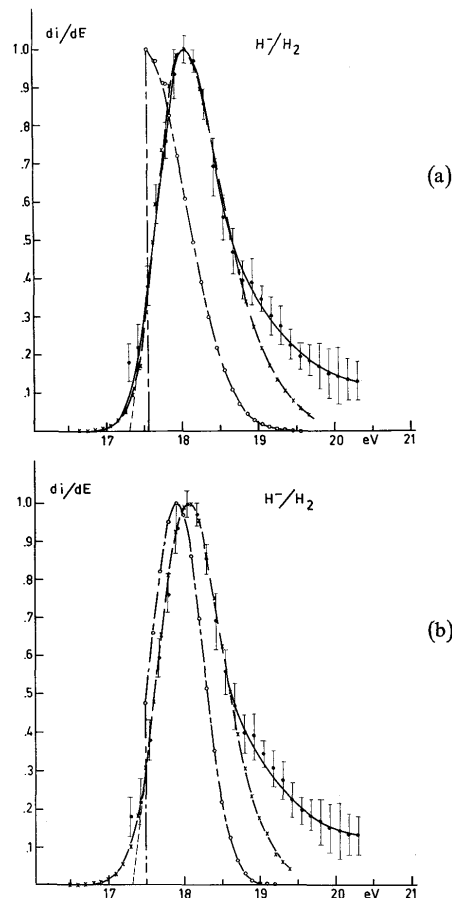


Fig. 6. First differential peak of H in H_2 (\bullet); (a) $f(a)$ -type ($-O-$), convoluted model ($-x-$); (b) $f(b)$ -type ($-O-$), convoluted model ($-x-$).



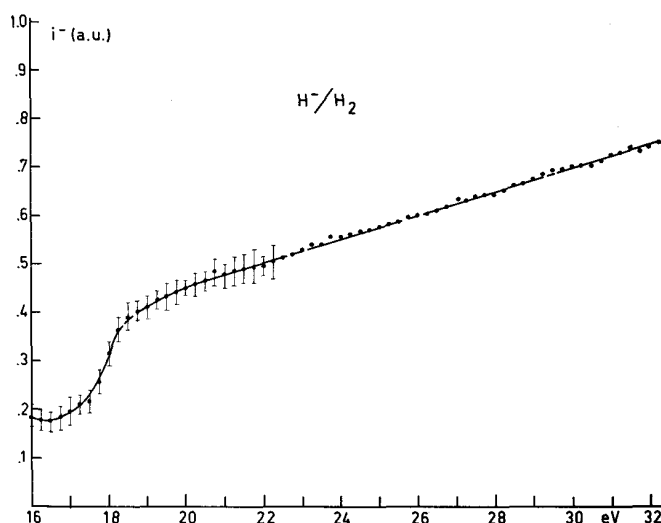
As it has been shown, for H^- no excited state exists²⁶. The only possible excited state when combining two 1S_g -terms, is $^1\Sigma_g^+$.

The electronic excited state of H_2 concerned in mechanism (1a) should not be the $(2p\sigma)^2 F^1\Sigma_g^+$ state²³. The ionic character of this state exists only at the vicinity of the second minimum of the E , $F^1\Sigma_g^+$ state²⁷: for a large internuclear distance this character disappears. In addition to this, in the energy range of interest the situation is complicated by the existence of a large number of states belonging to the same symmetry²³.

An ionization efficiency curve has been recorded over a wide energy range (Fig. 7). Within the limits of error, the negative ion current increases linearly with the electron energy in the range of about 20 eV up to 32 eV. The deconvoluted first derivative (Fig. 1b) is constant from 21 eV.

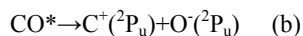
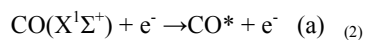
It follows that in this case, the excess energy function is a pure step-function followed by a straight line with positive slope.

Fig. 7. Direct IP efficiency curve over the range of 16 eV to 32 eV of H^- in H_2 .



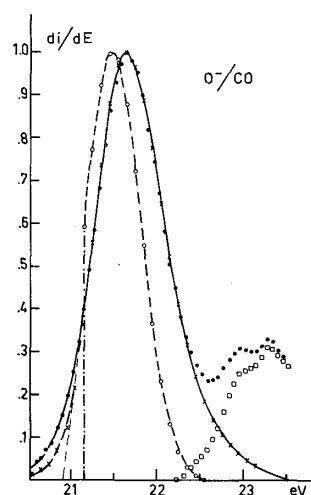
C. The O^- ion in CO

The first process observed in the first differential curve fits best an $f(b)$ -type convoluted model¹, as shown in Fig. 8, with a total KE width of 1.4 eV. The width at half-height is 0.70 eV, in good agreement with the 0.65 eV observed by deconvolution of the first derivative. The O^- ion appears without KE and no energy correction has to be made¹ for the threshold determined at (20.88 ± 0.02) eV, in good agreement with previous works (Table 1a). Taking $D(CO) = 11.108$ eV²³, $IP(C) = 11.264$ eV²⁴ and $EA(O) = 1.465$ eV²⁸, the calculated onset for the mechanism



is 20.907 eV. The combination of two 2P_u -terms gives rise to singlet and triplet $\Sigma^+(2)$, Σ , $\Pi(2)$ and Δ states¹.

Fig. 8. First differential peak of O^- in CO (\bullet); $f(b)$ -type (-O-), convoluted model (-x-). The curve obtained by intensity difference between the experimental peak and the convoluted model is shown (\square).



¹ Herzberg's notations are used to give the number of states belonging to the same symmetry.

According to Dunn's selection rules²⁹ concerning the excitation by electron impact on diatomic molecules, the $1,3\Sigma^- \leftarrow X^1\Sigma^+$ transitions are forbidden. From the twelve possible states, foreseen by the Wigner-Witmer correlation rules, ten states are observable according to the selection rules. If we assume that in our experiments all these possible CO excited states are reached, the seven states which are observed are reached in their repulsive part and it seems probable that in the Franck-Condon region the three remaining states only should be reached in their attractive part.

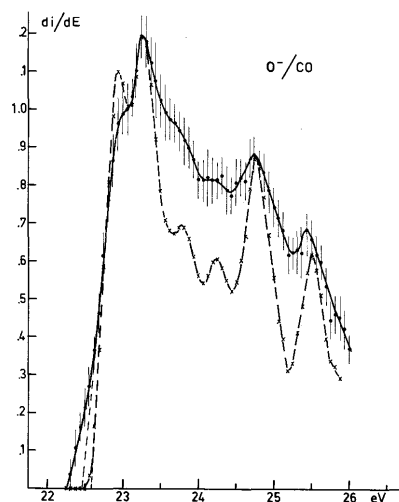
In the energy range of interest, the absorption spectrum of CO obtained by Tanaka³⁰ shows the existence of five unassigned series of bands, overlapping Rydberg series. These bands are designated by *P*, *Q*, *R*, *S* and *T*²³ or by P_i ($i = 1$ to 5) (ref. 30). However, there is not enough experimental evidence to suggest a correlation between some of these states and the three states which we postulate to be reached by the transitions in the attractive part of their potential energy curve.

Moreover, it is not possible, in the present case, to give an assignment to the lowest observed state giving rise to $C^+(^2P_u) + O(^2P_u)$.

By convolution of a theoretical model and also by deconvolution, the second peak is resolved and its threshold in both cases is 22.4 eV. This favours the assumption, implicit in the convolution, that the first differential of the first peak gets down to zero. Therefore, the threshold law for this process is probably a real step-function.

The curve obtained by subtraction of the first peak has been deconvoluted independently (Fig. 9). In this way the six other processes are clearly shown. The second onset and the following processes are not easily correlated with the appearance of the C^+ ion in an excited level and O^- in its ground state. The first electronic excited level $4P_g$ of the C^+ ion is at 5.33 eV²⁴ above the ground level. An excitation energy of 0.5 eV on the O^- ion is very unlikely³¹.

Fig. 9. First differential curve of the IP processes of *O* in CO above 22 eV; (●) experimental, (x) deconvoluted.

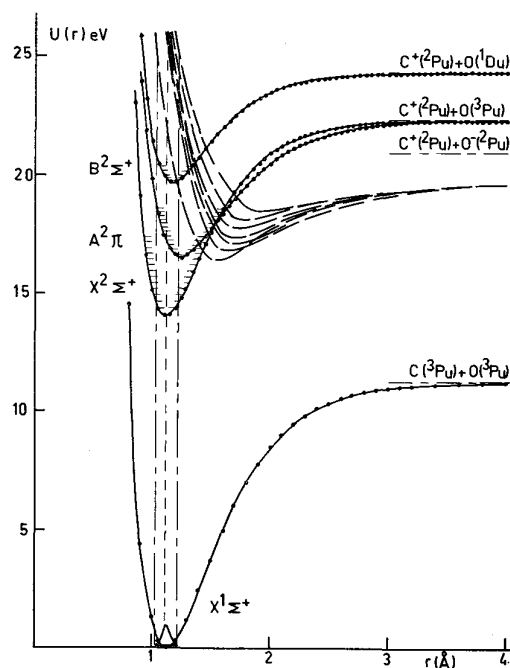


If it is accepted that for these ion-pair processes, the simple step-function assumption remains valid, the only interpretation of the successive processes observed, is that each of these corresponds to an excited state of the molecule which joins the same dissociation limit $C^+(^2P_u) + O(^2P_u)$ and belongs to one of the configurations foreseen by the Wigner-Witmer correlation rules. In all these processes the O^- ions appear with KE from threshold. On account of the Coulombic attraction at large internuclear distances, none of these states is expected to be completely repulsive.

The situation deduced from the experimental data and the previous discussion is schematically summarized in Fig. 10. The shape, in the Franck-Condon region, of the potential energy curve relative to the excited state which gives rise to the first observed ion-pair process is drawn taking into account the convolution data. The position of the six other potential energy curves are drawn considering the position of the second threshold and the following successive maxima. The data used for the ionized states of CO are taken from

Krupenie and Weissman³² and Guerin³³.

Fig. 10. Potential energy curves diagram of CO, CO⁺ (-●-) and CO*(-) as deduced from the discussion in Section 3c.



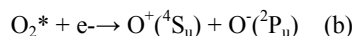
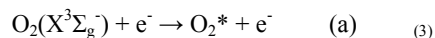
D. The O⁻ ion in O₂

The first ion-pair process giving rise to O⁻ in oxygen, was used previously as a reference for the electron energy scale calibration for the DA process of O⁻ in O₂². The photoionization value of (17.25±0.2) eV has been adopted: 0.2 eV is the reproducibility of the onset of the DA process.

The first peak is best fitted by an *f*(*b*)-type convoluted model (Fig. 11). The total KE width is 1.4 eV, the width at half-height is 0.65 eV and the maximum is shifted by 0.3 eV. By deconvolution the width at half-height of the first peak is 0.72 eV and the maximum is shifted by 0.1 eV. At the threshold the O⁻ ions do not carry away any KE. This is in agreement with the results of the KE analysis performed by Chantry and Schulz³⁴. No *f*(*a*)-type convoluted model¹ can be superposed to the first differential peak at 17.25 eV.

The model shows that at the maximum the O⁻ ion carries away 0.3 eV KE, in disagreement with the peak shape observed by Dibeler⁴ in better agreement with the curve obtained by Elder⁸. However, in both experiments, the discrimination effect of the mass spectrometers used, on the peak shape, is unknown.

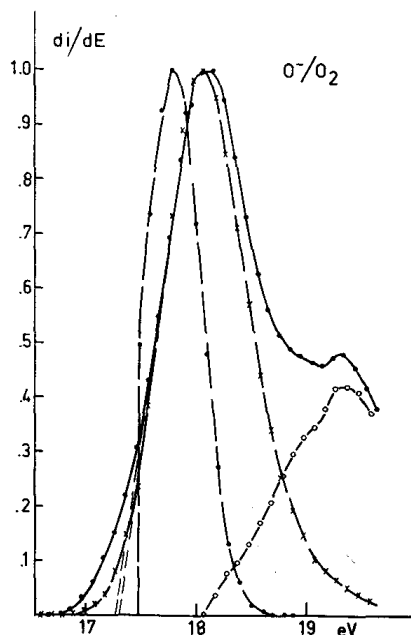
When D(O₂) = 5.080 eV²³, IP(O) = 13.614 eV²⁴ and EA(O) = 1.465 eV²⁸ are adopted to calculate the onset of the lowest energetic ion-pair process:



the threshold of the mechanism (3) is at 17.23 eV.

The combination of ⁴S_u-term with a ²P_u-term gives rise to triplet and quintet Σ⁻ and Π states. According to Dunn's electron impact selection rules²⁹, only the Σ_g⁻ ← X³Σ_g⁻ and Π_u ← X³Σ_g⁻ transitions are allowed. The process at 17.25 eV being observed by photon impact^{4,8}, the electronic transition which gives rise to it is governed by the optical selection rules allowing, in the most general case, only the ³Π_u ← X³Σ_g⁻ transition.

Fig. 11. First differential of the first peak of O^- in O_2 (●); $f(b)$ -type (-●-), convoluted model (x); the curve obtained by intensity difference is shown (○).



It is probable that the excited state O_2^* concerned in mechanism (3a) is the $^3\Pi_u$ state.

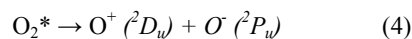
Three maxima are observed at (18.9 ± 0.2) eV, (19.2 ± 0.2) eV and (20.0 ± 0.2) eV in the deconvoluted curve. A shoulder at 18.9 eV is also present in the curve obtained by intensity difference between the first convoluted peak and the first differential efficiency curve of O^- in O_2 (Fig. 11). This fact favours the step-function threshold law, assumed by the convolution such as it is used.

Dorman⁶ determined an onset at (19.7 ± 0.1) eV; no unambiguous interpretation is proposed. Frost and McDowell²⁰ determined an unassigned "break" at 18.3 eV in the RPD ionization efficiency curve of O^- .

The three above-mentioned processes cannot be correlated with the formation of the O^+ ion in one of its excited levels. The lowest excited state of O^+ is at 3.325 eV²⁴ above the ground level. It is very likely that these ion-pair processes can be correlated with the $^3\Sigma_g^-$, $^5\Sigma_g^-$ and $^5\Pi_u$ states foreseen by the Wigner-Witmer correlation rules and converging to the dissociation limit at 17.25 eV. In the three last processes, the O^- ion is formed at threshold with KE.

A very sharp rising peak, completely resolved by deconvolution, has its threshold at (20.6 ± 0.2) eV. Previous works^{16,17,6} mentioned a threshold at (20.2 ± 0.2) eV and (20.4 ± 0.2) eV, respectively.

This onset is in good agreement with the calculated threshold for the mechanism



which is at $17.25 + 3.32 = 20.57$ eV. The O^- ion is probably formed without KE. The electronic transition takes place at the asymptote of an excited state which rises above the dissociation limit at or very close to the equilibrium internuclear distance of the ground state.

In the same group of peaks a second onset is determined at (21.3 ± 0.2) eV which cannot be ascribed to another mechanism: the first excited level above the 2D_u state, is the 2P_u level at 5.019 eV²⁴ above the ground state. This process is probably due to the mechanism (4) where the O^- ion carries away about 0.7 eV KE. Previously Frost and McDowell²⁰ mentioned a "break" at (21.22 ± 0.05) eV, assigned to the same mechanism.

These two last ion-pair processes are formed by the transition to excited states which have one of the symmetries obtained by combination of a 2D_u -term with a 2P_u -term, i.e. Σ^+ , Σ^- (2), Π (3), Δ (2) and Φ states with

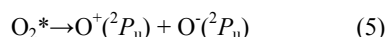
both singlet and triplet multiplicities.

Two reasons could be ascribed to the fact that not all of the above-mentioned states are observed.

Starting from the $X^3\Sigma_g^-$ ground state of O_2 , only transitions to ${}^{1,3}\Sigma_g^-$, ${}^{1,3}\Pi_u$ and ${}^{1,3}\Delta_g$ states are allowed by Dunn's selection rules²⁹. The $\Phi \leftarrow \Sigma_g^-$ transitions are not considered in that paper. Even with the help of these selection rules, it is not possible, within the frame of this work, to correlate two of these states with the two observed processes.

Moreover, several of these allowed states are, more than probably, attained in their attractive part only, by the Franck-Condon transition.

A third and last group of peaks shows four ion-pair processes, the first of which has a sharply rising onset at (22.5 ± 0.2) eV. To this threshold corresponds very probably the mechanism:



where the O^+ ion is formed in its second excited 2P_u level at 5.019 eV^{24} above the ground state. The minimum calculated threshold is $17.25 \pm 5.02 = 22.27 \text{ eV}$. Probably little or no KE is involved in this process.

The ion-pair processes observed at higher energies, i.e. $(23.6 \pm 0.2) \text{ eV}$, $(23.9 \pm 0.2) \text{ eV}$ and $(25.2 \pm 0.2) \text{ eV}$, respectively, are formed by electronic transitions up to higher excited states of O_2 converging to the dissociation limit at 22.27 eV . Kinetic energy is involved in these processes.

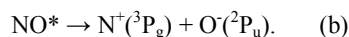
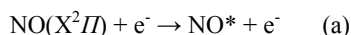
The combination of two 2P_u -terms gives rise to singlet and triplet $\Sigma^+(2)$, Σ , $\Pi(2)$ as well as to Δ states. As seen before, only transitions to ${}^{1,3}\Sigma_g^-$, ${}^{1,3}\Pi_u$ and ${}^{1,3}\Delta_g$ are allowed, i.e. probably at least six states have to be observed. Actually, only four processes are noticed. It is very likely that some of the above-mentioned states are reached in their attractive part by the Franck-Condon transition.

To summarize the previous discussion, the results are schematically drawn in Fig. 12, using the convolution and deconvolution data. For the potential energy curves of the ground state of O_2 and the five states relative to O_2^+ , in the energy range of interest, the data of Gilmore^{3,5} are used.

E. The O ion in NO

The initial peak of the first derivative of O^- appearing in NO by ion-pair formation is an $f(b)$ -type curve¹ with a total KE width of 2.0 eV (Fig. 13). The width at half-height is 1.12 eV and the maximum is shifted by 0.2 eV . By deconvolution the width at half-height is 0.90 eV and the maximum is shifted by 0.1 eV .

The negative ion is formed without KE and no correction has to be made on the threshold energy determined at $(19.6 \pm 0.3) \text{ eV}$, the DA peak having the same theoretical shape². This onset is in good agreement with the calculated threshold, using $D(\text{NO}) = 6.487 \text{ eV}^{23}$, $IP(\text{N}) = 14.54 \text{ eV}^{24}$ and $EA(\text{O}) = 1.465 \text{ eV}^{28}$ (calculated onset at 19.562 eV). The corresponding mechanism is very probably:



The combination of a 3P_g -term with a 2P_u -term gives rise to doublet and quartet Σ^+ , $\Sigma(2)$, $\Pi(2)$ and Δ states. Transitions from the ground state $X^2\Pi$ of NO to each of these states are allowed by the selection rules of Dunn²⁹ for heteronuclear diatomic molecules. From the twelve possible states only the transition to one of these is observed. The Franck-Condon transition should reach the other states below their dissociation limit. As for CO, Tanaka³⁰ observed Rydberg series over-lapping P_i bands in the energy range of interest. A priori, however, no assignment can be given to the first observed excited state.

The second process is resolved by the convolution as well as by the deconvolution process. Through both, an onset is determined at $(21.4 \pm 0.3) \text{ eV}$. As assumed in the convolution method, the first process threshold law is very probably a step-function.

Fig. 12. Potential energy curves diagram of O_2 , O_2^+ (-●-) and O_2^* (--) as deduced from the discussion in Section 3D.

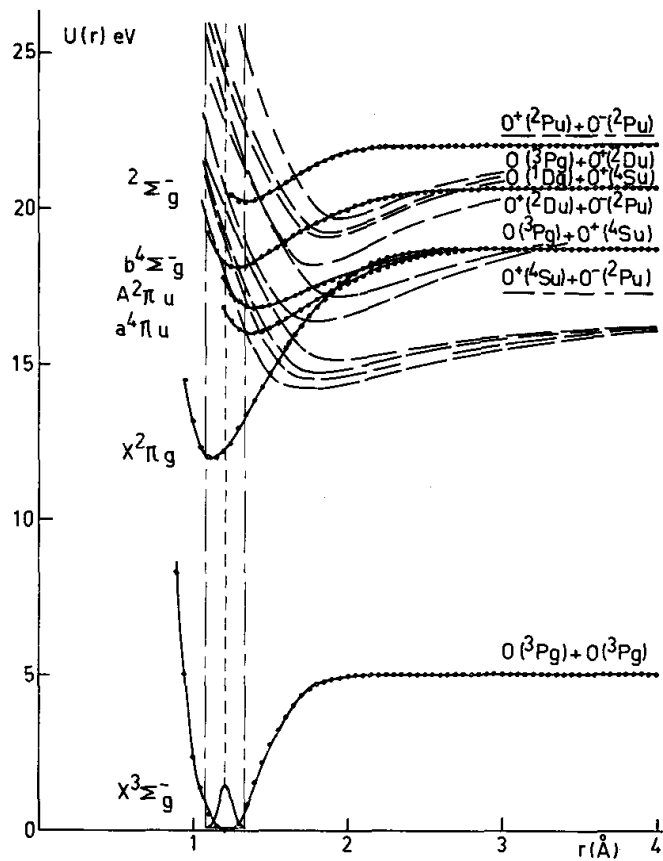
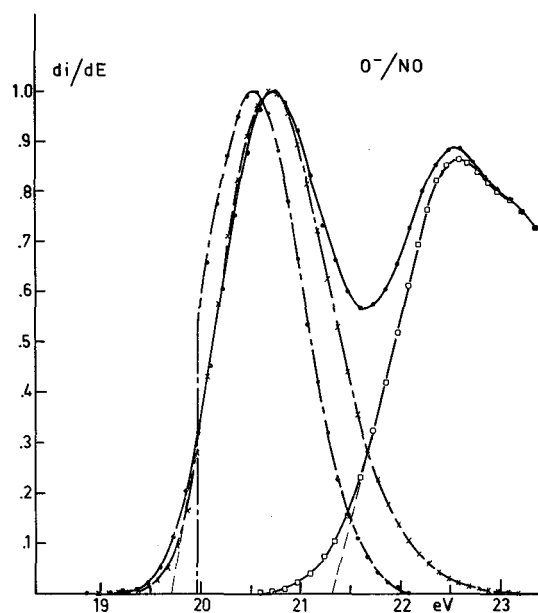
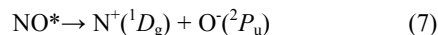


Fig. 13. First differential of the first peak of O^- in NO (·); $f(b)$ -type (-●-), convoluted model (-x-); the curve obtained by intensity difference is shown (D).



The second onset and the shoulder, which are better resolved by deconvolution, can be correlated with the appearance of the N^+ ion in its first excited 1D_g level, at 1.90 eV^{24} above the ground level. The theoretical onset for the mechanism:



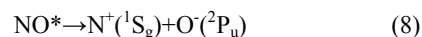
at 21.46 eV is in very good agreement with the experimental threshold.

This agreement does not exclude though the O^- ion from appearing through mechanism (6) from a transition to one of the states obtained by the Wigner-Witmer correlation rules. However, the intensity of the second process favours the interpretation of the onset at $(21.4 \pm 0.3) \text{ eV}$ by mechanism (7). It was not possible to apply the convolution process to the second peak, on account of the scarcely resolved shoulder at the high energy side of the peak.

The excited state concerned in this transition must be a doublet state, but the D_g - P_u terms give rise to $\Sigma^+(2)$, Σ , $\Pi(3)$, $\Delta(2)$ and Φ states. Transitions to these states all agree with the electron impact selection rules²⁹.

The shoulder observed at 23.1 eV is probably due to one of these doublet states which dissociates at the same dissociation limit, at 21.46 eV . In this case, however, the O^- ion will carry away a certain amount of KE.

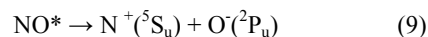
The fourth process, completely resolved by deconvolution, has its threshold at $(24.0 \pm 0.3) \text{ eV}$. A possible interpretation for this sharply rising peak is the formation of the O^- ion with N^+ in its second excited 1S_g level, at 4.054 eV^{24} above the ground state. The calculated onset of the mechanism



is at 23.616 eV . The KE carried away by the O^- ion could account for the discrepancy of $(0.4 \pm 0.3) \text{ eV}$. This is not precluded, even in the case of a sharply rising peak, as shown previously². The shape of the excited state potential energy curve in the Franck-Condon region could be responsible for the peak dissymmetry.

The molecular excited state of NO^* which dissociates at 23.6 eV must be a doublet Σ^+ or a Π state resulting from the combination of 1S_g - and 2P_u -terms.

The maximum at 25.7 eV , which is better resolved by deconvolution, should be due to the ion-pair process produced by an electronic transition to the repulsive part of either the $^2\Sigma^+$ or the $^2\Pi$ state converging to the same dissociation asymptote giving rise to $N^+(^1S_g) + O(^2P_u)$ at 23.6 eV . In this process KE is involved. The most probable interpretation of the ion-pair onset at $(25.5 \pm 0.3) \text{ eV}$ is the appearance of the O^- ion in its ground state with N^+ formed in the 5S_u level, at 5.85 eV^{24} above the ground state. The calculated threshold for the mechanism

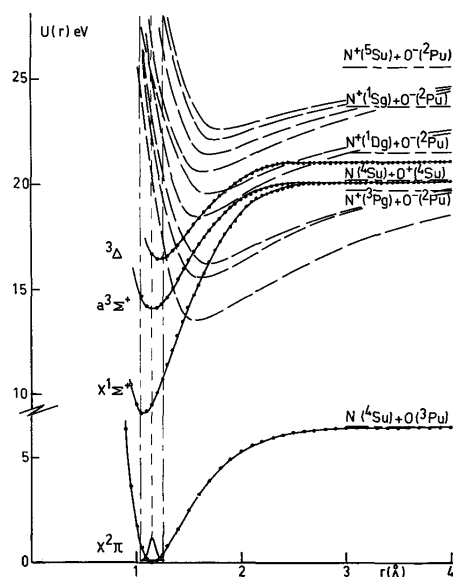


is at $19.57 + 5.85 = 25.42 \text{ eV}$, in good agreement with the experimental onset, within experimental error.

By combining a 5S_u -term with a 2P_u -term, doublet, quartet and sextet Σ and Π states are obtained. Here again all the transitions are allowed, and no criterion exists to assign any of these symmetries to the most stable state.

The process observed at 25.5 eV is followed by three peaks with an onset at $(26.4 \pm 0.3) \text{ eV}$, $(28.0 \pm 0.3) \text{ eV}$ and $(29.7 \pm 0.3) \text{ eV}$, respectively. None of these processes can be interpreted by the appearance of the N^+ ion in its 3D_u level, at 11.44 eV^{24} above the ground state.

Fig. 14. Potential energy curves relative to NO, NO⁺ (-●-) and NO* (- -) as deduced from the discussion in Section 3E.



The most probable origin of these ion-pair processes, is the electronic transition to the repulsive part of the potential energy curve of three NO* states which dissociate in N⁺ (⁵S_u) + O⁻ (²P_u) and have one of the symmetries deduced from the Wigner-Witmer correlation rules. In the three last processes KE must be involved. The ion-pair processes observed successively at 25.5 eV, 26.4 eV, 28.0 eV and 29.7 eV are likely to be correlated with the doublet and quartet Σ and Π states. The electronic transition to ⁶Σ⁺ and ⁶Π states would be characterized by a very low probability and cannot therefore be detected.

We have tried to summarize schematically the results of the preceding discussion in Fig. 14. For the first excited state, the convolution data are taken into account to draw the potential energy curve shape in the Franck-Condon region. The onsets and the maxima have been considered for the other states. The potential energy curves relative to the ground electronic state of NO and to X¹Σ⁺, a³Σ⁺ and ³Δ states of NO⁺ are drawn using the data of Gilmore³⁵.

4. CONCLUSIONS

This work has shown that a detailed examination of the ion-pair processes appearing in diatomic molecules can fruitfully be achieved mass spectrometrically, using a conventional ion source. The first differential of the ionization efficiency curves and their deconvolution reveal fine structures just visible in the direct ionization efficiency curves. The simultaneous use of both the convolution of theoretical models and the deconvolution of the ionization efficiency curves first derivative has shown, in most of the cases studied in this work, that the function expressing the cross-section dependence of ion-pair processes on the electron energy should be a step-function, almost near the threshold. This does not hold in the case of hydrogen.

An interesting feature of this study is that the same kind of information can be obtained from the shape of the first differential peak of an ion-pair process as well as from the shape of the DA processes cross section, i.e. (i) the KE distribution of the negative ion which depends on the shape in the Franck-Condon region, and on the relative position of the excited state potential energy curve concerned in the electronic transition, with respect to the ground state of the molecules and (ii) a non-arbitrary method for the determination of the threshold energy of an ion-pair process, occurring from a diatomic molecule.

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