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IONIZATION AND DISSOCIATIVE IONIZATION OF O_2 AFTER ELECTRON AND ION IMPACT

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Ionization and dissociative ionization of O_2 after electron and ion impact.

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Abstract

The ionization of O_2 was investigated by using charge exchange in a double mass spectrometer. The breakdown graph was constructed. A break in the electron impact ionization efficiency curve is explained as being due to ion-molecule reactions between excited O^+ ions formed in an ion-pair process, and O_2. It was shown that the cross sections must be very small for the reaction

$$O^+ ({}^4S) + O_2 \rightarrow O + O_2^+$$

since the cross sections for the corresponding reaction with Si^+ are small. Implications for the aeronomy are discussed.

Introduction

The most important method of determining the higher ionization potentials (IP) of molecules has hitherto been the study of the breaks in their electron impact ionisation efficiency (IE) curves. It is well known that also preionization and ion-pair processes can cause such breaks, but only recently has it been pointed out [1, 2] that breaks can be caused by ion-molecule reactions as well, although only one gas is present in the ion source of the mass spectrometer. It was shown that the breaks in the IE curves for methane and methyl halides occurring at about 19 eV are probably caused by such ion-molecule reactions.

This finding is important, because formerly the breaks in these cases were interpreted as being due to ionization of a $[2s_C]$ electron, although the real IP of this electron probably has a considerably higher value in methane and consequently also in other organic compounds. This IP has been the object of many quantum-mechanical calculations, which, in good agreement with our results, have all given much higher values than 19 eV. We have therefore started work on other molecules to try to find out whether their IE curves also contain breaks caused by ion-molecule reactions in the ion source.

In this paper such an investigation is described for O_2. To explain a break at high energy in the IE curve for this molecule it was necessary to perform a rather detailed investigation of the charge exchange processes between positive ions and O_2, and to study the breakdown graph of O_2^+.

The main difficulty of this investigation has been that the interesting processes in O_2 take place at comparatively high energies (above 16 eV). In this energy region the organic molecules, studied earlier [3 - 12], supply little information about the recombination energies (RE) of the positive ions used in the charge exchange experiments. This was mainly because the molecules were difficult to ionize by means of charge exchange in this energy region owing to the high IP of the $[2s_C]$ electron (about 24 eV). It was therefore necessary to perform a separate investigation of the recombination properties of F^+ using a molecule containing other atoms than only C and H. For this investigation CCl_3F was chosen.

The structure of the oxygen molecule

The structure of O_2 is very well known. A review was given by Gilmore [13] with potential energy curves for O_2 and O_2^+. The electron configuration and the IP's of the different electrons are given below together with the corresponding states of the O_2^+ ion

	K	K	$\sigma_g 2s^2$	$\sigma_u 2s^2$		$\sigma_g 2p^2$		$\pi_u 2p^4$		$\pi_g 2p^2$
States of O_2^+				$^2\Sigma_u^-$	$c^4\Sigma_u^-$	$^2\Sigma_g^-$	$b^4\Sigma_g^-$	$A^2\Pi_u$	$a^4\Pi_u$	$X^2\Pi_g$
IP's [14]	561	561	43.5	29.4		16.2		18.9		10.8
IP's [15]					24.6	20.2	18.2	16.9	16.1	12.1
IP's [16]			42		24	21.4	18.6			
IP's [17]						20.3	18.2		16.3	12.1

The IP's have been obtained by *ab initio* quantum-mechanical calculations [14], by spectroscopic investigations [13, 15] (mainly from Rydberg series [15, 18]), ultraviolet absorption [16] and photoelectron spectroscopy [17]. In the two latter cases our interpretation partly differs from that of the authors.

As the potential energy curves for oxygen are well known, the relative probabilities for ionization have been estimated by means of Franck-Condon factors for the spectroscopically known states [19, 20]. These factors have been plotted as a function of energy in Fig. 1a. Provided the electron transition probabilities do not differ too much, Fig. 1a gives a picture of the transition probabilities for ionization by use of electron or ion impact. However, the possibility of transitions to repulsive ion states has not been taken into consideration in Fig. 1a, since the potential energy curves for these states are unknown. In Fig. 1b we have therefore plotted our experimental transition probabilities for ionization (Q), which are the relative cross sections in the charge exchange experiments described later.

For transitions to the $^2\Sigma_g^-$ state, no calculations of Franck-Condon factors are available, for the potential energy curve for this state, given by Gilmore, is very uncertain. Therefore they have been estimated in Fig. 1a from the data obtained by Turner [17] (five vibrational levels between 20.31 eV and 20.80 eV). For the transitions to the $c\,^4\Sigma_u^-$ state, the Franck-Condon factors have been crudely estimated from Gilmore's curves.

It must be pointed out that it is not a priori evident that the Franck-Condon factors can be used in connection with charge exchange experiments. It has been pointed out [21] that vibrational excitation may be produced during the charge transfer, due to some additional translational-vibrational energy transfer. It is, however, evident from a comparison of the Franck-Condon factors in Fig. 1a and our cross sections with Si^+ and Kr^+ shown in Fig. 1b, that, at least to the extent that can be observed in our apparatus, the Franck-Condon principle seems to be valid for ionization by means of charge exchange.

Also the dissociation limits of O_2 are well known from its dissociation energy and the IP's and electron affinity of oxygen. The dissociation processes are given in Table 1 together with the corresponding minimum energies [13, 22-25].

Earlier mass-spectrometric investigations of O_2

Using electron impact, the IE curves and appearance potentials (AP) of ions from O_2 have been studied by several authors [22, 26 - 28]. The IE curve for O_2^+ from O_2 measured by Frost and McDowell and Brion shows breaks at 12.2, 16.3, 17.2, and 18.4 eV, corresponding to the onsets of regions with high transition probability in Fig. 1a. In addition, they observed a break at 21.3 eV that cannot be explained in this way. Below we will show that O_2^+ is unstable at this energy (measurements with Ne^+) and will therefore try to explain this break as being due to an ion-molecule reaction. The IE curve for O^+ from O_2, measured by Frost and McDowell [22], shows breaks at 17.3, 19.0, 20.4, 21.3, and 22.0 eV and the IE curve for O^- at 17.3 and 21.2 eV in agreement with the dissociation limits in Table 1. Evidently ion-pair processes occur at 17.3 and 21.3 eV.

Also the photo-ionization of O_2 has been investigated mass spectrometrically. Weissler et al [29] found a great number of intense peaks in the photo-ionization efficiency curves for O_2^+ and O^+ from O_2. These peaks do not correspond to the regions of high transition probability in Fig. 1a, and were therefore interpreted as being due to preionization. Elder, Villarejo, and Inghram [25] studied the production of O^+ and O^- at 17.28 eV and found the process to be of importance only up to about 18 eV in agreement with the predicted form of the potential energy curve for O_2^*. The importance of the preionization is confirmed by photo-ionization measurements without mass spectrometric analysis [30 - 32].

The difficulties in interpreting the electron impact data are summarized by Dorman, Morrison, and Nicholson [24] and by McGowan, Clarke, Hanson, and Stebbings [33] who point out the great importance of preionization and ion-pair processes.

Experimental results

a) Investigation of O_2

In order to investigate the mechanism behind the break at 21.3 eV, O_2 was bombarded with slow positive ions in a double mass spectrometer, described earlier [2 - 12], and the mass spectra were recorded. The results are shown in Table 2, where the sums of the peak heights are normalized to 100. The last column in the table gives the relative cross sections (Q) in arbitrary units. The pressure of the target gas was determined approximately at the inlet, using a Pirani gauge.

From Table 2 it is evident that extrapolation down to zero pressure results in a vanishing fraction of the molecule ions when bombarding with slow Ne^+ ions (RE 21.6 eV) or slow He^+ ions (RE 24.6 eV). At the same time, of course, the relative abundances of fragment O^+ increase.

This result is consistent with AP's of O^+ in Table 1 and also with results by Stebbings, Smith, and Erhardt [34]. These authers explain their results with He^+ by the assumption that first O_2^+ $(c^4\Sigma_u^-)$ is formed at 24.6 eV and that then predissociation to a repulsive state takes place. However, our results with Ne^+ cannot be explained in a similar manner, and therefore these transitions probably go directly to repulsive states.

It is also evident from Table 2 that bombardment with fast Ne^+ ions gives a non-vanishing fraction of molecule ions on extrapolation to zero pressure. This implies that at high velocities transfer of translational energy takes place to make possible transitions to the bonding $^2\Sigma_g^-$ state in the region between 20.3 and 20.8 eV.

b) Investigation of F^+

The F^+ ions can exist in three states $2s^2\ 2p^4\ {}^3P$, ^1D, and ^1S giving RE's 17.42, 20.01, and 22.98 eV, respectively [35]. In order to determine the statistical weights of the three states, CCl_3F was bombarded with Ne^+ and F^+ ions in the double mass spectrometer. The results are shown in Table 3 after normalization and reduction into monoisotopic peaks with respect to Cl. Also the electron impact mass spectrum and the AP's of the fragment ions [36, 37] are given in Table 3.

The strong increase of fragment $CClF^+$ in going from Ne^+ to F^+ must mean that this fragment is due mainly to RE 17.42 eV. RE 20.01 eV will be able to give fragments CCl_2^+ and CF^+ but is probably too high to give any appreciable amounts of $CClF^+$. Lastly, the RE 22.98 eV will cause the formation of fragments CCl^+ and Cl^+, but is considered to be too high to give any appreciable amounts of the other fragments.

From the mass spectra, it is possible to calculate the abundances of the different F^+ ions (cf. the corresponding calculation as to O^+ [4, 5]). This calculation presumes, of course, that the transition probabilities for ionization of CCl_3F are independent of energy in this energy range. The result is: 60% F^+ ions with RE 17.42 eV, 30% with RE 20.01 eV, and 10% with RE 22.98 eV. The F^+ ions were produced from SF_6 in an ion source with about 100 eV electrons.

Breakdown graph of O_2

The mass spectrum of O_2 as a function of the energy absorbed by the molecule during the charge transfer is shown in Fig. 1c. The AP's, 12.1, 18.7, and 20.7 eV, were taken from Table 1.

The results with F^+ ions require a detailed discussion. Fig. 1a and 1b shows that the probabilities for ionization of O_2 depend strongly on the RE. According to Gilmore's curves, there is no stable state of O_2 at 23 eV. Therefore the ionization at this energy must imply transitions to some repulsive state of O_2^+. It is therefore reasonable to assume that the probability for ionization here approximately equals the probabilities measured at 21.6 and 24.6 eV using Ne^+ and He^+ ions. Hence we take the mean of these Q-values as a measure of this probability. At 17.4 eV we use the Q-value obtained using F^+ ions as a measure of this probability since the probabilities at 20 and 23 eV evidently are comparatively small.

The probability for ionization at 20 eV is more difficult to estimate. The Franck-Condon factors assume high values between 20.3 and 20.8 eV, but the energy defect 0.3 eV is probably large enough to prevent charge exchange between F^+ (^1D) and O_2 with formation of O_2^+ ($^2\Sigma_g^-$) at low velocities of the F^+ ions.

This assumption is supported by our finding that when bombarding with Ne^+ ions (energy excess 0.7 eV) no O_2^+ ions are formed at low velocities. Thus, in this case, too, the charge exchange must imply formation of O_2^+ in some repulsive state, and hence we assume that the probability is about the same as at 23.0 eV.

The ordinate of the O^+ curve at 20.0 eV in Fig. 1c can now be calculated from the mass spectrum using F^+ ions, as the number of O^+ ions formed in the charge exchange at a certain energy is further proportional to the relative abundance of the F^+ ions with corresponding RE and to the probability for ionization of O_2 at this energy. Depending upon the values chosen for the different probabilities, the value of the ordinate will range between about 0.2 and 0.8. The uncertainty is mostly due to the small number of O^+ ions formed using F^+.

It must be remarked that in Fig. 1c the influence of the $^2\Sigma_g^-$ state has not been taken into account. This would probably cause a hump in the O_2^+ curve, but such a hump cannot be observed by use of the ion-impact method.

The discussion shows that the concept "breakdown graph" can hardly be used in the case of a diatomic molecule, owing to the gaps with low probabilities for ionisation. This is in contrast to the case of a polyatomic molecule, where the many states cause a high and roughly constant distribution function over a large energy range, and therefore the breakdown graph in this case gives a picture of the consecutive dissociations of the parent ion (cf. [3 - 12]).

Formation of O_2^+ at higher energies

From Fig. 1c it is evident that no stable molecule ions can be obtained at energies above 21 eV. Therefore, the breaks at 21.3 eV in Frost and McDowell's and Brion's IE curves cannot be due to O_2^+ ions formed in a primary process. The energy seems to be too high for an explanation by means of the $^2\Sigma_g^-$ state. Our hypothesis is therefore that this break is due to an ion-molecule reaction in the ion source. In this case the source of the O_2^+ ions must be the O^+ ions produced at 21.3 eV in the ion-pair process

$$O_2^* \rightarrow O^+(^2D) + O^-(^2P)$$

and therefore the break in the IE curve for O_2^+ at 21.3 eV is only a reflection of the break at the same energy in the IE curve for O^+. This picture is consistent with the fact that the break is more pronounced in Brion's curve than in Frost and McDowell's curve, and that Brion reports a higher pressure than Frost and McDowell.

To prove our hypothesis it is necessary to show that the O^+ ions formed at 21.3 eV are able to react with O_2 to give O_2^+, and also that the O^+ ions formed at lower energies cannot produce O_2^+. From Table 1 it is evident that below 21.3 eV (in the table the minimum energy 20.60 eV is given) O^+ ions are formed only in the ^4S state with RE 13.62 eV and that above 21.3 eV (20.60 eV) O^+ ions also are formed in the ^2D and ^2P states with RE's 14.98 and 16.94 eV (^2D) and 14.45, 16.67, and 18.64 eV (^2P) [35]. We will show below that at low velocities the O^+ (^4S) ions cannot and the O^+ (^2D) ions can react with O_2, giving O_2^+.

Charge transfer between O^+ and O_2 at low velocities

According to Fig. 1a the Franck-Condon factors are zero at 13.62 eV. Therefore we expect that the cross section for charge exchange between O^+ (^4S) and O_2 is very small. Since we cannot produce O^+ ions exclusively in this state, we used an indirect method for the proof.

When bombarding with Si^+ the relative cross section, Q, was very small (Table 2). This ion exists in two states, ^4P with RE's 13.47 and 9.35 eV and ^2P with RE's 8.15 eV and lower. It has been shown earlier [4] that the ^4P state is abundant and that RE 13.47 eV can give charge exchange with large cross sections. We furthermore performed a special investigation of methane, shown in Table 4, which demonstrates the importance of RE 13.47 eV in Si^+. The small cross sections with Si^+ also at high velocities in Table 2 prove that when the RE of an incident ion is somewhat higher than 13.47 and the velocity is low, charge exchange with O_2 cannot take place with any appreciable probability.

Kr^+ has RE's 14.00 and 14.67 eV and the cross section is still smaller than with Si^+. The small O^+ peak is due to high metastable states of Kr^+ with RE's about 18 eV [3, 35, 38].

The experiments with Si^+ and Kr^+ thus prove that slow O^+ (^4S) ions cannot produce charge exchange with O_2 with any appreciable degree of probability.

According to Fig. 1a the Franck-Condon factors are high at 16.67 and 16.94 eV. Therefore we expect the cross sections for charge exchange between O^+ (^2D) or O^+ (^2P) and O_2 to be large. That O^+ and O_2 are able to react has already been shown in beam experiments by Stebbings et al [39, 40]. To prove that this charge exchange takes place also at thermal velocities of the O^+ ions, we studied the secondary charge exchange processes in the collision chamber at increased pressure. The increase of O_2^+ ions with increasing pressure when bombarding with Ne^+ and He^+ ions, although at very low pressures only O^+ ions are formed, proves that a reaction occurs. We have shown that the O^+ (^4S) ions do not react and therefore it is necessary for at least the O^+ (^2D) ions to do so. In the case of bombardment with Ne^+, it must be assumed that the O^+ (^2D) ions are formed in a process endothermic by 0.4 eV, which is not unreasonable if the small cross section is taken into consideration.

The results at high pressures in Table 2 thus prove that slow O^+ (^2D) ions and probably also slow O^+ (^2P) ions can react in charge exchange with O_2.

Upper atmosphere implications

The present results are of considerable importance in connection with aeronomy, since the reaction

$O^+ + O_2 \rightarrow O + O_2^+$

is important in determining the electron and ion densities of the atmosphere (cf. review articles by Paulson [41], Fite [42], and Danilov and Ivanov-Kholodnyi [43]). The reaction has been studied by a number of authors, who have obtained quite different values for the reaction rate [39, 40, 44 - 46]. In view of our results this is not unexpected. As O^+ in the ground state can react with O_2 only to a very limited extent, the determinations of the reaction rates are strongly influenced by the contents of excited states in the ion beams. These contents will vary from one experiment to another, for they depend not only upon the gas used for production of O^+ [3, 4], but also upon the excitation conditions [47, 48] (cf. [42]). This is probably enough to explain the different values obtained for the reaction rates.

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Table 1. The minimum energies for the ionic dissociation processes in O_2 giving O^+ ions.

	Products	Minimum energy (eV)
$O_2 \longrightarrow$	$O^+ (^4S) + O^- (^2P)$	17.28
	$O^+ (^4S) + O (^3P)$	18.73
	$O^+ (^2D) + O^- (^2P)$	20.60
	$O^+ (^4S) + O (^1D)$	20.70
	$O^+ (^2D) + O (^3P)$	22.05
	$O^+ (^2P) + O^- (^2P)$	22.30
	$O^+ (^4S) + O (^1S)$	22.92
	$O^+ (^2P) + O (^3P)$	23.75
	$O^+ (^2D) + O (^1D)$	24.04
	$O^+ (^2P) + O (^1D)$	25.72
	$O^+ (^2D) + O (^1S)$	26.24
	$O^+ (^2P) + O (^1S)$	27.94

Table 2. Mass spectra of O_2 obtained in charge exchange with incident positive ions of low kinetic energy (KE) as a function of pressure.

Incident ion	KE eV	Pressure microns	O_2^+	O^+	Q
He^+	18	400	53.5	46.5	3.4
	18	200	24.8	75.2	0.9
	18	100	11.8	88.2	0.7
	18	50	7.1	92.9	0.7
F^+	25	400	95.8	4.2	16.0
	25	200	96.6	3.4	11.5
	25	100	96.9	3.1	8.4
	25	50	96.8	3.2	8.2
	100	30	96.6	3.4	14.6
	300	35	97.1	2.9	16.3
	900	40	95.8	4.2	13.6
Ne^+	25	400	61.4	38.6	0.8
	25	200	37.6	62.4	0.3
	25	100	18.4	81.6	0.2
	25	50	7.1	92.9	0.2
	100	200	40.0	60.0	0.3
	100	100	23.2	76.8	0.2
	100	50	12.4	87.6	0.1
	900	200	53.7	46.3	0.3
	900	100	37.8	62.2	0.1
	900	50	28.7	71.3	0.1
Si^+	30	30	100.0	0.0	0.1
	100	30	98.7	1.3	0.2
	900	30	98.3	1.7	0.3
Kr^+	35	50	62.7	37.3	0.05
	100	50	80.0	20.0	0.06
	300	50	86.2	13.8	0.07
	900	50	89.2	10.8	0.12
Xe^+	40	50	100.0	0.0	1.8
	100	50	100.0	0.0	2.9
	300	50	100.0	0.0	2.7
	900	50	99.9	0.1	3.3

Table 3. Mass spectra of CCl_3F obtained in charge exchange with Ne^+ and F^+ ions of low kinetic energy (KE). The electron impact mass spectrum and the AP's of the resulting fragments are also given.

Incident ion	KE eV	CCl_3^+	CCl_2F^+	CCl_2^+	Ions $CClF^+$	CCl^+	Cl^+	CF^+	F^+	Q
Ne^+	28	§	§	13.0	1.8	37.8	8.7	38.7	0.0	0.9
	100	§	§	10.2	2.6	38.7	11.7	36.8	0.0	0.6
	900	§	§	8.2	4.0	39.6	16.9	31.3	0.0	0.5
F^+	17	§	§	11.5	56.0	9.0	3.6	19.9	0.0	1.4
	35	§	§	9.9	55.3	9.9	5.0	19.9	0.0	0.9
	100	§	§	9.9	49.1	12.4	7.4	21.2	0.0	0.8
	300	0.0	10*	11.8	46.8	12.1	8.9	20.4	0.0	0.8
	900	§	§	12.5	51.6	11.8	7.7	15.4	0.0	1.2
e [36]		2	100	3	11	8	13	8	0.1	
AP [36]		13.8	12.3	18.9	17.0	21.2	21.2	19.1	29.5	
AP [37]		12.8	12.0	-	17.4	-	-	-	-	

§ not measured

* not included in the normalization

Table 4. Mass spectra of CH_4 obtained in charge exchange with CO^+ and Si^+ ions of low kinetic energy (KE). Inlet pressure is 50 μ. The CH_4^+ ions obtained when bombarding with Si^+ can be produced only by RE 13.47 eV [9]. Comparison with CO^+ (RE 14.0 eV) shows that the cross section is not small.

Incident ion	KE eV	Ions CH_4^+	CH_3^+	CH_2^+	CH^+	Q
CO^+	40	63.0	32.7	4.2	0.1	12.4
	100	64.8	31.4	3.7	0.1	10.3
	300	62.2	33.8	3.9	0.1	8.6
	900	59.2	37.4	3.2	0.2	7.3
Si^+	40	62.4	32.9	4.7	0.0	2.7
	100	65.8	30.1	4.1	0.0	2.4
	300	64.3	31.4	4.3	0.0	2.2
	900	64.3	32.1	3.6	0.0	2.5

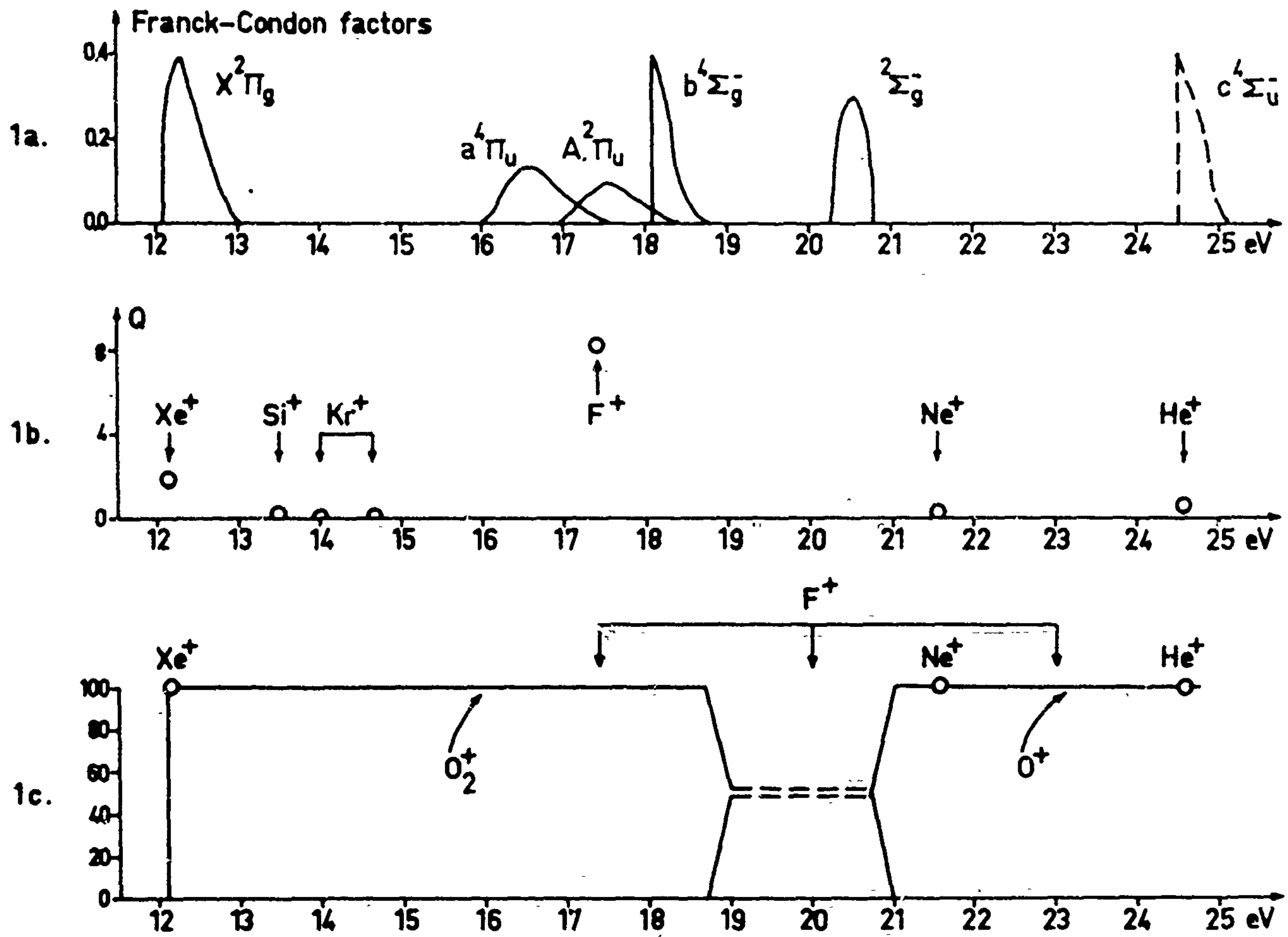

Fig. 1. a) Franck-Condon factors for ionization of O_2.

b) Relative cross sections for charge transfer between different positive ions and O_2.

c) Mass spectrum of O_2 as a function of energy (eV).

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13. ABSTRACT

The ionization of O_2 was investigated by using charge exchange in a double mass spectrometer. The breakdown graph was constructed. A break in the electron impact ionization efficiency curve is explained as being due to ion-molecule reactions between excited O^+ ions formed in an ion-pair process, and O_2. It was shown that the cross sections must be very small for the reaction

$$O^+ ({}^4S) + O_2 \rightarrow O + O_2^+$$

since the cross sections for the corresponding reaction with Si^+ are small. Implications for the aeronomy are discussed.

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14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Mass spectra						
Charge exchange						
O_2						
Dissociation of oxygen molecule ion						
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