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The Far Ultraviolet Absorption Spectrum of Oxygen

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The far ultraviolet absorption spectrum of oxygen has been photographed under high dispersion in the region 1300–650A. The bands are explained as going to the various excited states of O_2^+ as limits and are attributed to the removal of $v\pi$, $\omega\pi$ and $x\sigma$ electrons, respectively, from the normal state of O_2. The results strongly support Mulliken's assignment of the visible O_2^+ bands to the transition $^4\Sigma_g^- \rightarrow {}^4\Pi_u$. The distances of the $^4\Pi_u$ and $^4\Sigma_g^-$ states of O_2^+ from the ground state of O_2 are given as 16.1 and 18.2 volts, respectively, with possible errors of about a tenth of a volt. The appearance and nonappearance of strong electronic series going to known ionization potentials are also discussed.

THE ultraviolet absorption spectrum of oxygen begins with the Schumann-Runge bands.[1] Under normal conditions these start around 1970A and extend toward shorter wave-lengths until they are concealed by a strong continuous absorption. The intensity of this absorption diminishes to zero at about 1350A. Below this there is a system of absorption bands extending from 1250A which are evident only when relatively high pressures of O_2 are used. On the short wave-length side of this system are the Hopfield bands[2] which extend down to 680A. Unfortunately no emission bands of O_2 are known in the ultraviolet. The authors and others have tried several methods to obtain the Hopfield bands in emission, but without success. It is therefore very desirable to work out the absorption spectrum of O_2 as completely as possible. The original photographs of Hopfield were probably not taken under sufficiently high dispersion to allow a good analysis to be made. The work was therefore repeated under much higher dispersion, the Lyman continuum being used as a source of continuous radiation.

The instrument used was a two-meter grazing incidence vacuum spectrograph having a dispersion of about 2A/mm in the region 1200–600A. The discharge tube and the methods of obtaining the spectra have been described in a previous article.[3] The Hopfield bands in oxygen appear at such extremely low pressures that it was found convenient when taking the low pressure pictures to use a mixture of oxygen and helium in order that a sufficient pressure for the satisfactory operation of the discharge tube could be obtained. The helium was originally purified by passing it over charcoal cooled with liquid air. Mixtures varying from one to ten parts of oxygen in a hundred parts of helium were used to obtain plates at different pressures. The mixture was admitted into the spectrograph through the discharge tube by means of a fine capillary. It was pumped out continuously through the main pumps. The conditions were such that the partial pressures of oxygen varied from about 0.01 mm to 0.001 mm and the length of the absorbing path was about 1.5 meters. To obtain the absorption bands above 1000A, oxygen was admitted without dilution at a pressure of about 0.1 mm.

The photographs obtained as described above are shown in Fig. 1. A comparison of this absorption spectrum with those of N_2 and H_2O in the same region showed that no bands due to these possible impurities were present in appreciable amounts. It was found, however, that excited oxygen was always present in small quantities in the spectrograph, as strips of polished copper introduced into the instrument became tarnished in the course of an exposure. However, control experiments showed that none of the absorption bands which are reported here could be attributed to absorption in such excited molecules.

The emission spectrum of H_2[4] is a convenient comparison spectrum for the wave-length determination of the bands above 1000A. For the bands below 1000A emission lines in the continuum which were identified as due to highly

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[1] S. W. Leifson, Astrophys. J. **63**, 73 (1926).

[2] J. J. Hopfield, Astrophys. J. **72**, 133 (1930).

[3] G. B. Collins and W. C. Price, Rev. Sci. Inst. **5**, 423 (1934).

[4] H. H. Hyman, Phys. Rev. **36**, 187 (1930).

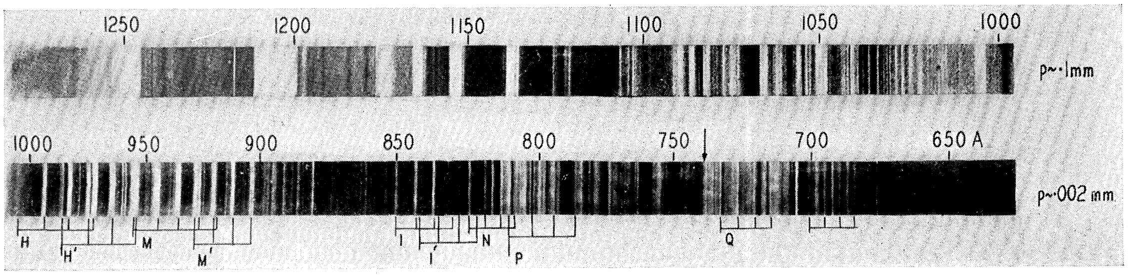

FIG. 1. The far ultraviolet absorption spectrum of oxygen.

ionized states of O and N were used as standards, their wave-lengths being taken from Edlén.[5] The accuracy of the measurements on the sharp bands is probably such that their frequencies can be given to within ±5 cm^{-1}. The errors in the measurement of broad and diffuse bands and those which fall close to emission lines in the continuum are considerably greater than this. The inaccuracy of these determinations may be at first thought rather large, but it must be remembered that the factor $\Delta\nu/\Delta\lambda$ at 800A is about twenty-five times as great as it is around 4000A. A large number of plates taken under different conditions were measured and a reasonable average of the wave-lengths so obtained was taken.

BANDS ABOVE 1000A

It has been shown[6] that the far ultraviolet absorption spectra of a number of molecules consist of various electronic series, with or without vibrational patterns, which go to a limit agreeing fairly well with the ionization potention of the molecule as determined by electron impact. Some molecules show strong Rydberg series going to the minimum ionization potential, while others show strong series going to one or more higher ionization potentials, the series going to the minimum ionization potential being apparently very weak. Examples of the latter type are the far ultraviolet absorption spectra of O_2, NO, N_2 and CO. It can be said at least that the electronic series and ionization continua corresponding to the first ionization potentials of these molecules do not appear at the low pressures which are usually adequate to bring them out in other molecules (cp. C_2H_2, H_2S, CH_3I). The bands going to the other ionization potentials of these molecules, i.e., Hopfield's Rydberg series[7] in nitrogen and the shorter wave-length bands of oxygen to be discussed here exhibit more usual behavior. Without attempting any explanation of this, we wish to record here the empirical facts.

The bands in oxygen above 1000A come out at relatively high pressures (0.1 mm). They are of the character of electronic series going to a limit between 12 and 12.5 volts. The value 12.5 ±0.1 volts is the first ionization potential of O_2 as obtained by electron impact.[8] A more exact value depending on the extrapolation over a very small range of the vibrational levels of the $^2\Pi_u$ excited state of O_2^+ to its heat of dissociation turns out to be 12.2±0.1 volts.[9] Actually no bands of the long wave-length set we obtained were observed below 1018A (12.1 volts). The first bands in the region 1250–1200A are somewhat predissociated, probably due to the proximity of the potential curve of the $\sigma^2\pi^3\pi^3$, $^3\Sigma_u$ state or other predicted states. They are very strong and apparently not accompanied by any vibrations, which is in agreement with the fact that 'r' and 'ω' are not very greatly different for the ground states of O_2 and O_2^+. The shorter wave-length bands are very much weaker and

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[5] B. Edlén, Zeits. f. Physik **85**, 85 (1933).

[6] R. S. Mulliken, Phys. Rev. **46**, 144 (1934); H. J. Henning, Ann. d. Physik **13**, 599 (1932); W. C. Price, Phys. Rev. **47**, 419, 444, 510, 788 (1935); J. Chem. Phys. **3**, 256, 365 (1935).

[7] J. J. Hopfield, Phys. Rev. **36**, 789A (1930).

[8] J. T. Tate and P. T. Smith, Phys. Rev. **39**, 270 (1932).

[9] R. S. Mulliken and D. S. Stevens, Phys. Rev. **44**, 720 (1933).

though they appear to converge to a limit $\sim$1015A$\equiv$12.15 volts, they could not be arranged in any Rydberg series. Even if it had been possible to do this, the intensities of the electronic series would have been very unusual, as the long wave-length bands are very much stronger than the shorter wave-length bands (i.e., the intensities fall off much more rapidly than for the electronic series going to an ionization continuum which have been observed in other molecules). No ionization continuum could be found for these bands though a slight weakening of the background was observed to extend from 1105A toward shorter wave-lengths (probably due to weak transitions to repulsion curves).

As the internuclear distance of the ground state of O_2^+ is less than that of O_2 one would expect bands going to the former state as a limit to be shaded toward the violet. This is only true of some of the bands we observe. Some are shaded toward the red and some are so narrow that it is difficult to say in what direction they are shaded.

A very similar situation occurs in NO. The bands which might be regarded as the first members of a set going to the minimum ionization potential were obtained by Leifson.[1] They are strong and form two good vibrational progressions for which 'ω' is not much different from that in the ground state. We have photographed the NO bands at shorter wave-lengths and found that the bands go to a limit which is close to the value 9.4 volts determined by electron impact. However, the upper members lose the simplicity of the lower ones. They suffer great diminutions in intensity and cannot be arranged in Rydberg series. Even at the highest pressure used ($\sim$0.3 mm) they do not give an ionization continuum.

Another example of what has been discussed above is nitrogen. The first ionization potential of nitrogen is accurately known to be about 15.55 volts[10] and thus one might expect a Rydberg series with an ionization continuum starting at 794A to appear in absorption (little vibrational structure would be expected as 'r' and 'ω' are not greatly different for the ground states of N_2 and N_2^+). This has not been found by Hopfield.[11] In more recent work by one of us (P) at higher pressures, a continuum has been found in this region but the bands going to it cannot be identified with the type of bands one would expect to approach the ground state of N_2^+. Their interpretation is as yet uncertain.

In CO as in NO the first few states are found fairly strongly with frequencies differing little from the ground state. Hopfield and Birge[12] have obtained the bands as far as 920A but do not get any higher series members. The absorption past the first ionization potential (14.1 volts $\equiv$875A) has been done by Henning.[6] Discrete bands were found as far down as 783A and no continuum corresponding to the first ionization potential was observed. However, Henning reports evidence of a second ionization potential which is close to Mackay's[13] value of 15.6 volts for the second I.P. of CO.

While it is disappointing not to be able to get direct spectroscopic evidence of the first ionization potentials of the above molecules, it is considered important to point out the instances in which such evidence cannot be easily obtained.

BANDS FROM 1000–650A

The Hopfield bands extend from a little above 1000A to as far down as 650A. The pressures at which they appear are so low that all the longer wave-length bands are practically entirely absent. They thus correspond to bands which have enormously high transition probabilities. They were found to consist of fairly short vibrational progressions having about four or five members. The various vibrational progressions are indicated in Fig. 1 and listed in Table I. There is a break in the absorption between 900 and 850A. The bands start again on the short wave-length side of this with diminished intensity. Around 800A the bands overlap so much that little can be done with them. This is exactly what one would expect if the bands were due to the vibrational progressions of various terms of an electronic series going to an ionization potential.

On the basis of evidence to be presented below the bands are interpreted as transitions

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[10] R. S. Mulliken, Phys. Rev. **46**, 144 (1934).

[11] J. J. Hopfield, Phys. Rev. **36**, 789A (1930).

[12] J. J. Hopfield and R. T. Birge, Phys. Rev. **29**, 922A (1927).

[13] C. A. Mackay, Phys. Rev. **24**, 327 (1924).

TABLE I. *Table of frequencies of various progressions in the Hopfield bands in* O_2.

I	ν	$\Delta\nu$	*I*	ν	$\Delta\nu$	*I*	ν	$\Delta\nu$	*I*	ν	$\Delta\nu$
	H			*H′*			*N*			*N′*	
3	99630		4	101440		8	121064			———	
		1070			1090			899			
8	100700		8	2530		8	121963			———	
		1020			1050			867			
10	1720		10	3580		7	122830			———	
		1000			1010			830			
8	2820		7(b)	4590		4	123670			———	
	M			*M′*			*P*			*Q*	
8b	104470		8	107150		10	123330		8	136559	
		1030			1020			1340			1166
10	5500		9	8170		8(o)	4670		6	7725	
		1010			960			1290			1121
9	6510		8	9130		6	5960		4	8846	
		950			860			1250			1088
7	7460		6	9990		4	7210		2	9924	
		900									
3(o)	8360										
	I			*I′*			*V*			*W*	
3	117200		2	118500		4	142670		5	143300	
		1012			1030			1180			1150
5	8212		4	9530		4	3850		6	4450	
		983			990			1120			1100
6	9195		5	120540		3	4970		4	5550	
		950			970			1070			
4	120145		3	1510		2	6040				
					950						
			1	2460							

from the ground state of O_2 to upper electronic states which approach as limits the excited states of O_2^+. Two of these states can be identified as the upper and lower states of the visible bands of O_2^+. Their term values with respect to the ground state of O_2 are found here to be ~18.2 volts and ~16.1 volts with a probable error of 0.1 volt. It has not yet been possible to analyze the structure of the visible O_2^+ bands but Mulliken[14] has tentatively assigned them to the transition $^4\Sigma_g^- \rightarrow {}^4\Pi_u$ identifying the $^4\Pi_u$ state with the second ionization potential (16.1 volts) determined by electron impact. Our results are in complete agreement with this assignment.

The interpretation of the far ultraviolet absorption spectra of some molecules as going to excited states of the ion has already been applied by Mulliken[14] to Hopfield's Rydberg series in nitrogen which go to the well-known A', $^2\Sigma_u^+$ state of N_2^+ as a limit. The difference between these bands and the ones we shall describe is that while in N_2 each electronic state gives only one band ('*r*' and 'ω' are changed very little by the excitation), in oxygen each electronic state has a vibrational progression associated with it ('*r*' and 'ω' are changed very considerably by the excitation). Rathenau[15] has interpreted the far ultraviolet absorption spectra of CO_2 as going to excited states of CO_2^+, but no correlation with the emission bands of CO_2^+ has yet been made.

The data on the Hopfield bands in oxygen are given in Table I. The lettering scheme is such that bands in the groups *HIJ*···, *MNO*···, *PQR*··· belong to Rydberg series approaching the limit characteristic of each particular group. On account of their similarity in vibrational frequencies, intensity distribution, appearance, etc., the progressions "*H*" and "*I*" are assigned to the same Rydberg series. If their first members are introduced into a Rydberg formula, the limit so obtained is ~130,300 cm^{-1}. In the same way "*H′*" and "*I′*" are assigned to another Rydberg series which has a limit ~131,400 cm^{-1}. This

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[14] R. S. Mulliken, Rev. Mod. Phys. **4**, 56 (1932).

[15] G. Rathenau, Zeits. f. Physik **87**, 32 (1933).

agreement between the limits is considered fair in view of the uncertainty of the identification of the first members of the progressions and the possible departure of the electronic states from a Rydberg series. Their average, 130,800 cm^{-1}, corresponds to an ionization potential of 16.14 volts which is in good agreement with the value 16.1 volts obtained by Tate and Smith[8] by electron impact for the second ionization potential of oxygen.

The vibration frequencies of these bands approach that of the lower state of the visible bands of O_2^+. This is especially so in the "*I*" progression where incidentally the measurements are best. For this state ω_e turns out to be ~ 1042 cm^{-1} and $x_e\omega_e \sim 15$ cm^{-1} as compared with the values 1037.2 and 11.1 for O_2^+. Further the intensity distribution of the bands is approximately what one would expect for such a transition. The internuclear distance of normal O_2 is 1.204A. That of the lower state of the visible bands of O_2^+ is not accurately known but is probably ~ 1.4A. Thus one would expect the first band to be weak, the second and third somewhat stronger and subsequent members weaker. This is found to be the case. Under the dispersion used here the bands appear as doublets. The maxima of the two components are separated by about 75 cm^{-1}. The minima in between these is a very narrow region of transparency not more than a few wave numbers broad. All the members of the *A* and *B* systems were found to have this structure.

From the above it is indicated that the lower state of the visible O_2^+ bands has a term value ~ 16.1 volts with respect to the ground state of O_2. We shall later show that the bands approaching the upper state due to absorption from normal ${}^3\Sigma_g^-$, O_2 are single headed and go to a limit ~ 18.2 volts. The $\Delta V = 18.2 - 16.1 = 2.1$ volts agrees with the observed $\nu_e = 2.05$ volts of the visible bands of O_2^+. It thus appears that our results strongly support Mulliken's assignment of the transition ${}^4\Sigma_g^- \rightarrow {}^4\Pi_u$ to these bands.

With regard to the probable nature of the upper levels of the *H*, *I*, *J* series a few things may be said. The states which go to the state of O_2^+ should include $({}^4\Pi_{\frac{1}{2}})nx$, $({}^4\Pi_{\frac{1}{2}})nx$, $({}^4\Pi_{3/2})nx$ and $({}^4\Pi_{5/2})nx$ with probably $\Omega - s$ type coupling. If nx is $nx\sigma$ then the states would correspond to ${}^5\Pi$ and ${}^3\Pi$. The question of selection rules is rather complicated but transitions to some components of both states (all of ${}^3\Pi$) should occur.

Two other strong progressions *M* and *M′* were found in the bands between 1000 and 900A. These appear at somewhat shorter wave-lengths than the *HH′* progressions and have smaller values of 'ω.' They are of the same character as the *H*, *I*, *J*··· bands having two components separated by a fine line. Only one of the "*N*" progressions could be found at shorter wave-lengths; *N′* is apparently lost in the confusion produced by the overlapping of a number of electronic states in the region 820–770A. By introducing *M* and *N* into a Rydberg formula one obtains 16.5 volts for the ionization potential of these bands. On account of the fact that the value of $\omega_e \sim 915$ cm^{-1} for *N* is close to that of the ${}^2\Pi_u$ state of O_2^+ ($\omega_e = 898.9$) it seems possible that the bands go to this state as a limit. From the ultraviolet bands of O_2^+ the ${}^2\Pi_u$ state is known to be 4.73 volts above the ground state of O_2^+. With the value of Mulliken and Stevens for the ionization potential of O_2, the distance of the ${}^2\Pi_u$ state of O_2^+ relative to the ground state of O_2 is $12.2 + 4.73 = 16.9$ volts. While the value 16.5 volts which we have obtained has a possible error of a few tenths of a volt, it is doubtful whether it could be raised as high as 16.9 volts. The other excited states of O_2^+ which are predicted in this region[16] can probably be ruled out as limits of our series since they are produced by the removal of a $w\pi$ electron from the metastable states ${}^1\Delta_g$ and ${}^1\Sigma_g^+$ of O_2. However it is conceivable that the excitation could be accompanied by an interval rearrangement of the $v\pi_g^2$ group. One could then get the ionic states ${}^2\Phi_u$, ${}^2\Pi_u$ (corresponding to the removal of one $w\pi_u$ from $\sigma_g^2\pi_u^4\pi_g^2$, ${}^1\Delta_g$) or the ${}^2\Pi_u$ corresponding to the removal of one electron from the $\sigma_g^2\pi_u^4\pi_g^2$, ${}^1\Sigma_g^+$ state. While the probability of such a process is small it cannot be entirely neglected.

In connection with the ionization potential of the *MNO* system we might look for an ionization continuum. Such a continuum is apparently found. It starts fairly sharply around $740\mathrm{A} \equiv 16.7$ volts which seems close enough to our value of the ionization potential of this system to be

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[16] R. S. Mulliken, Rev. Mod. Phys. **4**, 56 (1932).

identified with it. However, the possibility that the continuum is a dissociation continuum cannot be eliminated. If the latter is the case then the continuum may be explained as transitions to repulsion curves giving the same products of dissociation as the *H* or *M* systems.

A third set of bands *Q* appears in the continuum mentioned previously. These are quite sharp and good measurements could be made on them. They are single headed and are shaded toward the red. The values of $\omega_e \sim 1205$ cm^{-1} and $x_e\omega_e \sim 20$ cm^{-1} indicate that the electronic state is approaching the upper state of the visible O_2^+ bands for which $\omega_e = 1198.1$ cm^{-1} and $x_e\omega_e = 17.8$ cm^{-1}. As has been previously mentioned, Mulliken has tentatively designated this state as $^4\Sigma_g^-$. This is supported by the fact that the bands are single headed. The intensity distribution of the bands is different from that of the *H* and *M* bands. The first member of the progression is strongest and subsequent members become gradually weaker. This indicates that the internuclear distance of the excited state is not greatly different from the ground state of O_2.

A progression marked *P* which is very similar to the *Q* progression can be picked out at longer wave-lengths. The first band is strong single headed and shaded towards the red. It is very similar to the first band in the *Q* progression. Good measurements could not be made on the subsequent members of the progression as they are partially obscured by the overlapping in the region around 800A. Introducing *P* and *Q* into a Rydberg formula we obtain 18.25 volts as the ionization potential of the *PQR* system. This is probably a little too high, as ω_e and *D* are somewhat greater for the *P* progression than the *Q* progression.

The only predicted states of O_2^+ which are about 18 volts removed from the ground state of O_2 are the $\sigma_g\pi_u^4\pi_g^2$, $^4\Sigma_g^-$ and $^2\Sigma_g^-$ states. It thus seems reasonable that the *PQR*··· bands are approaching one of these (probably $^4\Sigma_g^-$). The fact that ω_e and $x_e\omega_e$ for *Q* are close to their values in the upper state of the visible O_2^+ bands indicates that this state can probably be identified as the limit and thus it corresponds to the configuration $\sigma_g\pi_u^4\pi_g^2$, $^4\Sigma_g^-$.

Two other progressions labeled *V* and *W* were found in the region 700–670A. The analysis of these bands is uncertain. The bands in *W* appear to be double headed with the apparent exception of that at 144,450 cm^{-1}. A few strong isolated bands believed to belong to oxygen were found at 112,890, 122,350 and 141,820 cm^{-1}. The last band is extremely strong.

The configuration of normal O_2 is $\sigma_g^2\pi_u^4\pi_g^2$, $^3\Sigma_g^-$. The bands which go to the first ionization potential of O_2 are due to the excitation of a π_g electron. Those going to the excited Π states of O_2^+ are due to the excitation of a π_u electron and those going to the Σ states due to the excitation of a σ_g electron. Thus in the far ultraviolet absorption spectra of O_2 we have evidence of the excitation of all three types. Theoretically the low energy states of O_2^+ can be obtained in a very simple way by the removal of an electron from each of the outer orbits of O_2. This is apparently what actually happens in the far ultraviolet absorption spectra of oxygen.

While the data given in this paper are not as accurate as could be wished for, the authors believe it is the best that will be available for some time. The difficulties of working in this region are considerable and even with the high dispersion used here the $\Delta\nu/\Delta\lambda$ factor is so large that the accuracy of the measurements is limited considerably. However, it is significant that where the accuracy of the measurements is greatest (i.e., in the *I*, *N* and *Q* systems) the interpretation is followed most closely. The work yields very plausible term values for some of the electronic states of O_2^+ relative to the ground state of O_2. It also gives an insight into the nature of the far ultraviolet absorption spectra of molecules and their relations to the results of electron impact experiments. As this is a subject on which there is as yet little experimental data the work is considered valuable in this respect.

In conclusion the authors wish to thank Professor G. H. Dieke for his advice and encouragement and Professor R. S. Mulliken for much valuable criticism of the manuscript.

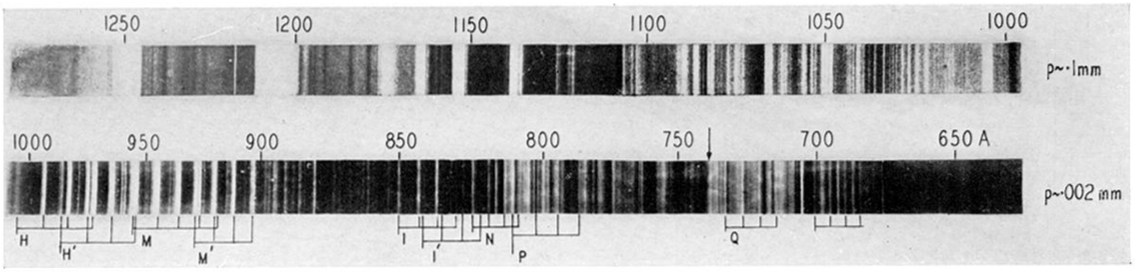

Fig. 1. The far ultraviolet absorption spectrum of oxygen.