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SIMULTANEOUS IONIZATION AND DISSOCIATION OF OXYGEN AND INTENSITIES OF THE ULTRA-VIOLET O_2^+ BANDS

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Abstract

Observations by Hogness and Lunn, Smyth and Stueckelberg, showing that O^+ is formed from the neutral molecule by a single impact of about 20 volts, are explained from the potential energy curves of the molecule and ion. These have been obtained from a method given by P. M. Morse, and from the empirical law $r_0^3\omega_0 = 3000\text{A cm}^{-1}$. The intensities of the ultra-violet O_2^+ bands have been calculated from the same curves and are in good agreement with experiment.

Different observers[1] have found ionization potentials between 13.5 and 15.5 volts corresponding to the formation of stable O_2^+. Mackay[2] was the only observer who found two distinct ionization potentials, at 12.6 and 16.1 volts. Above 20 volts Hogness and Lunn[3] found O^+ ions as products of single impacts. Smyth and Stueckelberg[4] confirmed this result and found in addition, that neon ions (having an energy of 21.6 volts) react with neutral O_2 molecules in collisions of the second kind, forming O^+. The conclusion is, therefore, that the potential at which O^+ is formed from O_2 lies between 20 and 21.6 volts.

These facts have been compared with the scheme of potential energy curves for the different states of O_2 and O_2^+. The data for these curves have been obtained from the tables of Birge[5] and of Mulliken.[6] The calculation has not been done by a power series in $(r-r_0)$ as usual, but by a method given by Morse in the foregoing paper.[7] The equilibrium separation (r_0) is not known experimentally for the O_2^+ levels, because the rotation structure has not yet been analysed. The values of r_0 for these states have been obtained by an empirical law which relates ω_0 and r_0, also described in the paper by Morse.

Applying the principle of Franck concerning the most probable transitions between electronic states in molecules[8] to the curves of Fig. 1 we see that the following reactions may be expected: at 13.5 volts: $O_2 \rightarrow O_2^+$ (in the normal state of O_2^+); at higher voltages transitions to the excited stages of

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[1] Franck u. Jordan, Anregung v. Quantensprungen p. 273.
[2] Mackay, Phys. Rev. **24**, 319 (1924).
[3] Hogness and Lunn, Phys. Rev. **27**, 732 (1926).
[4] Smyth and Stueckelberg, Phys. Rev. **32**, 779 (1928).
[5] Birge, Molecular Spectra in Gases, p. 232.
[6] R. S. Mulliken, Phys. Rev. **32**, 186 and 761 (1928).
[7] P. M. Morse, Phys. Rev. **34**, 57 (1929).
[8] J. Franck, Trans. Far. Soc. **21**, part 3 (1925).

O_2^+ will occur, such as at 20 volts: $O_2 \rightarrow O_2^{+\prime}$ (in a higher vibrational state of the electronic state labelled with Π?); at 20.3 volts: $O_2 \rightarrow O + O^+$. The most probable transition reaches this upper $^2\Pi$ state at its dissociation limit. The $O_2^{+\prime}$ will therefore immediately dissociate into O and O^+.

Comparing these values with the observed data the formation of 0^+ as a primary product at 20.3 volts agrees with the observed facts, but we have no good explanation for the different values for the ionization potential forming stable O_2^+.

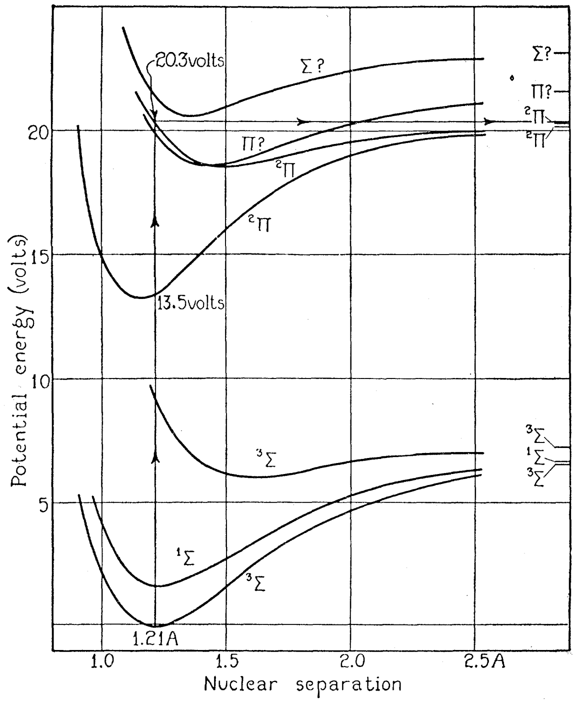

Fig. 1. Potential energy curves for O_2 and O_2^+. Energy in volts and nuclear separation in Angstrom units.

Taking into account the inexactness of the Franck principle, as suggested from quantum mechanics by Condon,[9] we expect that below 20.3 volts a considerable number of O_2^+ is formed with a vibrational energy near dissociation. We expect therefore that besides the O^+, formed by a primary process, there will occur some secondary O^+. In the experiments mentioned above there has not been found any evidence of this. This may suggest that the r_0 of this state is a little too small.

The relative value of the r_0 in this state with respect to the normal state of the O_2^+ can be checked by calculating the intensities of the transitions between these states. This has been done by a method given by Condon.[10]

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[9] E. U. Condon, Phys. Rev. **32,** 858 (1928).

[10] E. U. Condon, Phys. Rev. **28,** 1182 (1926).

Figure 2 shows the two potential energy curves on larger scale and the vibration levels associated with them. Taking as the most probable transition

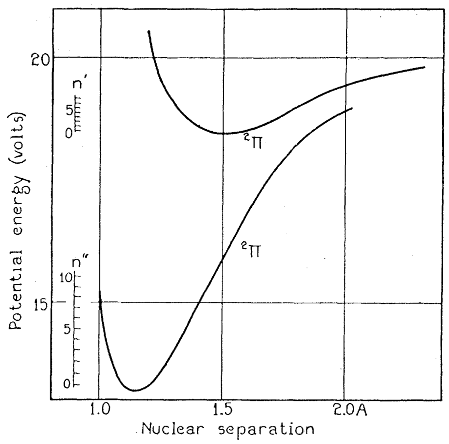
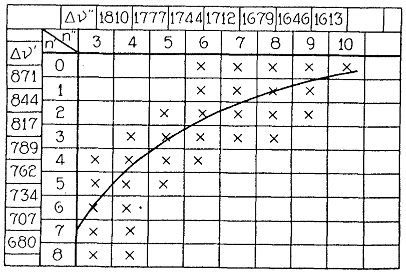


Fig. 2. Potential energy curves and vibration levels for $^2\Pi \rightarrow {}^2\Pi$ bands (ultra-violet O_2^+ bands). Energy in volts, nuclear separation in Angstrom units.

the one which leaves position and momentum of the nuclei unchanged during the transition we obtain the curve in Fig. 3. The observed bands as found by Johnson[11] are marked with crosses. As the centre of gravity of the ob-



	$\Delta\nu''$	1810	1777	1744	1712	1679	1646	1613		
$\Delta\nu'$	$n' \backslash n''$	3	4	5	6	7	8	9	10	
871	0				×	×	×	×	×	
844	1				×	×	×	×		
817	2			×	×	×	×	×		
789	3		×	×	×	×	×			
762	4	×	×	×	×					
734	5	×	×	×						
707	6	×	×							
680	7	×	×							
	8	×	×							

Fig. 3. Bandheads observed by Johnson marked by ×, and curve of maximum intensity as calculated from Fig. 2.

served bands coincides with the calculated curve, we have an additional confirmation for the chosen values of r_0, and therewith for the potential of 20.3 volts.

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[11] R. C. Johnson, Proc. Roy. Soc. **105A,** 683 (1924).