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New O_2^+ Bands. Dissociation Energy of O_2^+ and Ionization Potential of O_2

R. S. MULLIKEN AND D. S. STEVENS, *Ryerson Physical Laboratory, University of Chicago*

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Three new bands are reported in the first negative and several in the second negative system of O_2^+. The numbering of the vibrational levels of the normal state of O_2^+, hitherto in doubt, is definitely established. The observed ionization potentials I of O_2 at 12.5 and 16.1 volts are discussed. From the known O_2^+ energy levels it is shown that the dissociation energy D of O_2^+ cannot be less than 6.0 volts; by extrapolation from the known levels we get 6.54 volts. The latter value, however, would require 12.11 volts as the ionization potential of O_2. We suggest $D=6.45 \pm 0.1$ and $I=12.2\pm 0.1$ volt as a reasonable compromise (making D and I consistent, as they must be in reality) between the ionization potential and band spectrum data.

A. NEW O_2^+ BANDS; VIBRATIONAL NUMBERING

THE O_2^+ band spectrum contains two band systems; the first negative bands, which lie mainly in the visible and (probably) the infrared, and the second negative bands which extend through the visible and throughout the ultraviolet to below λ2000.[1, 2] The rotational structure of the first negative bands has never been analyzed, although it has been suggested that they may be $^4\Sigma^-_g \rightarrow {}^4\Pi_u$.[2] It is certain at any rate that they have no state in common with the second negative bands.

The second negative bands, whose rotational structure has been analyzed,[3] are of the type $^2\Pi \rightarrow {}^2\Pi$. In all probability their final state is the $^2\Pi_g$ normal state of O_2^+ and the bands are $^2\Pi_u \rightarrow {}^2\Pi_g$. The vibrational numbering of this system has never been satisfactorily established as regards v'', although the v' numbering is definitely known. This is because, on account of a large difference between r_e' and r_e'', bands having small v'' occur only for fairly large v' and these are weak and lie near λ2100, making them difficult to photograph. The only published data and photographs for the region near λ2100 in O_2^+ are those of Ellsworth and Hopfield.[4] Their reproduced photographs show bands of the system as far as λ2100 or perhaps as far as λ1975, but the authors give data only as far as λ2184 and state that the bands at shorter wave-lengths are too weak to measure.

Since a knowledge of the v numbering of the normal state of O_2^+ is necessary for an accurate knowledge of the values of r_e, ω_e and D (energy of dissociation) of O_2^+ and has a bearing on the ionization potential of O_2, we have taken new photographs of the O_2^+ spectrum under moderate dispersion with the object of photographing as many bands as possible, especially in the λ2100 region. (A description of the discharge tube used in this work will be published elsewhere by one of us.) In this way we have found several new bands of the second negative system, some near λ2100, others in the visible region.

We have also found three new bands which have the same structure as the first negative bands and extend the observed wave-length range of this system in both directions. Data on these bands are given in Table 1, together with v' and v'' assignments consistent with those now in use for the previously known bands of the system.

Our results on the second negative bands confirm the v'' assignment of Birge, which is that used by Ellsworth and Hopfield.[4] The new bands we have measured are given in Table I, with the values of v' and v'' which we believe to be correct.

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[1] Cf. W. Jevons, *Report on Band Spectra of Diatomic Molecules* (Published by the Physical Society, London, 1932), for data and literature.

[2] R. S. Mulliken, Rev. Mod. Phys. **4**, 51 (Fig. 48) and 82 (Table 29) (1932). It should be noted that the v numbering and resulting constants, as given in references 1, 2, are based on the present work.

[3] D. S. Stevens, Phys. Rev. **38**, 1292 (1931).

[4] V. M. Ellsworth and J. J. Hopfield, Phys. Rev. **29**, 79 (1927).

TABLE I. *Bands of O_2^+ newly found or measured by us. (All data refer to heads, and are in cm^{-1} in vacuo.)*

v',v''	ν	v',v''	ν
A. Bands of the second negative system			
15,0	48536 dif 48334 dif	0,10	21368 21177
14,0	48042 dif 47824 dif	1,11	20714 20496
13,0	47520 47329	0,11	19855 19655
12,0	46969 46745	0,12	18367 18182
11,0	46383 46197	1,13	masked 17606
11,1	44559 44375	1,14*	16381 masked
*B. Bands of the first negative system.***			
3,0	**19972**	0,1	15574
2,0	18878	0,2	14581
1,0	17751	0,3	**13606**
0,0	16589	0,4	**12669**

* Others may also be present at this end of the system, masked by first negative bands.

** The measurements (cm^{-1} in vacuo) refer to the *most obvious head* in each case. The data are from Frerichs' paper,[5] except for the new bands (0,3), (0,4), and (3,0). Each most obvious head appears to be accompanied by several others, namely, one fainter head displaced about 20 cm^{-1} towards smaller frequencies, as already noted by Frerichs, and two or three strong, but not always well-marked heads (or possibly accidental accumulations of lines) displaced towards larger frequencies.

(The errors of measurement, which are fairly large, can be judged by the lack of constancy in the measured interval between the two heads of each band in Table I.) The bands (11,0), (12,0), and (13,0) are clear and definite, while (14,0) and (15,0) are weak and diffuse-looking on our plates, but probably genuine. No bands beyond (15,0) can be distinguished. Conceivably this and the diffuseness of (14,0) and (15,0) are the result of a Stark effect in the strong fields used to produce the O_2^+ bands.

It is of especial interest that the (11,0), (12,0) and (13,0) bands are also easily visible and measurable (with results which, we find, check ours) on the reproduction given by Ellsworth and Hopfield, even though these authors did not give measurements for them. The present measurements on these bands agree within the experimental error with values calculated by extrapolating from the previously measured series (6,0) to (10,0). This result disposes of the supposition of Ellsworth and Hopfield that the bands, not measured by them, which we identify as (11,0) to (13,0) belong to new progressions with lower v'' values than any of the measured bands. It was as a matter of fact just this supposition of Ellsworth and Hopfield that raised the question about the v'' numbering which, we hope, is now settled.

Specifically, the question which we had to decide was whether the series of bands which we call $(v',0)$ really has $v''=0$ or whether it might be that they have $v''>0$. Our data, together with earlier data, give an unbroken series of $(v',0)$ bands from $v'=6$ to $v'=15$. If $v''>0$ were correct for this series of bands, for instance if $v''=1$, then another series with v'' really zero should also appear and, as one sees by plotting all the known bands on a Condon parabola, at least a few of this series should be intense enough to be plainly visible in the region of the bands which we call (11,0) to (15,0). Actually, no such extra bands are to be seen on our plates, and we conclude that what we call $v''=0$ really is so.

The v'' numbering here established disagrees with that deduced by one of us and by Stueckelberg on the basis of the observed vibrational intensity distribution and the Franck-Condon principle.[6] The disagreement is, however, disposed of by the fact that these intensity considerations were based on an assumed value of r_e' (about 1.5A) which differs considerably from the later determined actual value (1.41A)[3] and because of other uncertainties in the $U(r)$ curves used.

The wrong v'' numbering just mentioned (two units too large) was adopted by one of us[3] in connection with the analysis of the O_2^+ bands. Hence the v'' numbering in that paper and the molecular constants and equations which depend

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[5] R. Frerichs, Zeits. f. Physik **35**, 686 (1926). Although Frerichs gives probable band *origins* in his summarizing table, the heads can be found from his other tables.

[6] R. S. Mulliken, Phys. Rev. **32**, 213 (1928); E. C. G. Stueckelberg, Phys. Rev. **34**, 66 (1929).

on this should be changed. For example, the equation for B'' given there should be altered to:

$$B''=1.592-0.009v''.$$

These changes have already been included in the constants and figures of references 1 and 2.

B. Dissociation Energy of O_2^+ and Ionization Potentials of O_2

Measurements of the ionization potential of O_2 long gave conflicting results. Recent accurate measurements of Tate and Smith,[7] however, give two potentials, one at 12.5 and one at 16.1 volts (stated probable error ±0.1 volt) in exact agreement with earlier measurements by Mackay, whose results on ionization potentials of other gases have proved unusually reliable. The existence of two potentials, near 12.5 and near 16.1 volts, may then be considered as well established. The potential 12.5 volts doubtless corresponds to the energy required to remove a π_g electron from the normal state of O_2, which is . . . $(\sigma_g)^2(\pi_u)^4(\pi_g)^2$, ${}^3\Sigma^-{}_g$, to give the normal state of O_2^+, . . . $(\sigma_g)^2(\pi_u)^4(\pi_g)$, ${}^2\Pi_g$.

The potential at 16.1 volts may reasonably be interpreted as corresponding to the energy required to remove a π_u electron from normal O_2 to give O_2^+ in the state . . . $(\sigma_g)^2(\pi_u)^3(\pi_g)^2$, ${}^4\Pi_u$. A $U(r)$ curve for such a state (which *may* be the lower state of the first negative bands of O_2^+) is sketched in Fig. 48 of reference 2. It should be noted that, although the configuration $(\pi_u)^3(\pi_g)^2$ must give several states ${}^4\Pi_u$, ${}^2\Pi_u$, ${}^2\Phi_u$, ${}^2\Pi_u$, ${}^2\Pi_u$, just the first two of these are to be expected if an electron is removed from *normal* O_2, in which the $(\pi_g)^2$ group is in the particular condition ${}^3\Sigma^-{}_g$. The remaining states ${}^2\Phi_u$, ${}^2\Pi_u$, ${}^2\Pi_u$ correspond to ${}^1\Delta_g$ and ${}^1\Sigma^+{}_g$ conditions of the group $(\pi_g)^2$. The ${}^4\Pi_u$ state should be lower than the corresponding ${}^2\Pi_u$ state, which is probably the upper state of the second negative bands of O_2^+ and which should be excited at a higher potential. Although $v=0$ of this ${}^2\Pi_u$ is only 4.73 volts above that of the normal state of O_2^+, one expects electronic excitation produced by electron impact to be accompanied with high probability by strong vibrational excitation, even to the point of dissociation (cf. reference 2, Fig. 48). This is in agreement with the observations of several writers who have found that O^+ ions begin to be produced from O_2 at about 19 to 20 volts (cf. Stueckelberg).[6]

The energy required to dissociate and ionize unexcited O_2 so as to give unexcited $O^+({}^4S)$ $+O({}^3P_2)$ is exactly known: it is 18.65 volts. This is the sum of the ionization potential of O (13.56 volts for ${}^3P_2 \rightarrow {}^4S$) and the energy of dissociation of O_2 (5.09 volts for O_2, ${}^3\Sigma^-{}_g \rightarrow 2$ O, ${}^3P_2$). If from the value 18.65 volts we subtract 12.5 volts as the ionization potential of O_2, the remainder, 6.15 volts, should be the energy of dissociation, D, of $O_2^+({}^2\Pi_g)$ into $O({}^3P_2)+O^+({}^4S)$.

An independent estimate of D for O_2^+ can be made from data on the second negative O_2^+ bands. Theory shows that both the upper (${}^2\Pi_u$) and lower (${}^2\Pi_g$) electronic states of these bands are permitted to, and almost certainly would, give unexcited $O({}^3P_2)+O^+({}^4S)$ on dissociation. [Assumption of excited O (${}^1D$ or ${}^1S$) on dissociation runs counter to strict theoretical rules. If we assume excited $O^+({}^2D$ or ${}^2P)$ we get, on using data for the total energy of excitation plus dissociation of excited O_2^+, based on the second negative bands, only 3.2 or 1.6 volts for the dissociation of O_2^+, into unexcited $O+O^+$, values which are ridiculously low.]

With the v'' numbering established here, the energy interval from $v''=0$ of normal $O_2^+({}^2\Pi_{\frac{1}{2}g})$ to $v'=0$ of excited $O_2^+({}^2\Pi_u)$ is 4.73 volts, while the energy interval up to the last level $(v'=15)$ for which we have observed a band is 5.99 volts. (Note that for the ${}^2\Pi_u$ state, since it is of case *b* type,[3] the sub-levels ${}^2\Pi_{\frac{1}{2}}$ and ${}^2\Pi_{1\frac{1}{2}}$ fall together.) If we extrapolate the frequencies of the series of observed bands (6,0) to (15,0), we find that they converge approximately linearly toward a limit at 6.54 volts. Since the extrapolation beyond the last observed level is only 0.55 volt, our result should probably be not far from the correct value of D for the process $O_2^+({}^2\Pi_{\frac{1}{2}g}) \rightarrow O({}^3P_2)+O^+({}^4S)$. The corresponding value for D of the upper, ${}^2\Pi_u$, level is 1.81 volts. These values are somewhat higher than those (6.15 and 1.42 volts)[2] which we get from the ionization potential of O_2, using 12.5 volts for the latter. The disagreement is, however, within reason.

If we accept the D obtained from the ultra-

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

violet bands as correct, the ionization potential of O_2 becomes 12.11 volts. In view of the general downward tendency in measured ionization potentials of molecules as the technique of measurement is improved,[8] it seems quite possible that the value 12.1 volts for O_2 may prove to be correct. The possibility of such downward shifts in measured ionization potentials may be ascribed in part to the action of the Franck-Condon principle, which often makes ionization with $v>0$ more probable than ionization with $v=0$, so that strong ionization sets in only gradually and at some distance above the true minimum ionizing potential. On the other hand it may be, in view of the fact that D values obtained by linear extrapolation are nearly always high, that the value $D=6.54$ volts is a little too high. We would therefore suggest as a reasonable compromise the following mutually consistent estimates for D of O_2^+ and the ionization potential of O_2: 6.45 ± 0.1 and 12.2 ± 0.1 volts.

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[8] Consider, e.g., the results of Tate and associates[7] on N_2 and C_2H_2, as compared with earlier work; also J. T. Tate, P. T. Smith and A. L. Vaughan, Phys. Rev. **43**, 1054A (1933).