

good for this nucleus ($\text{Be}^8 + \text{H}$). It seems very unlikely that B^9 should be even more stable than is indicated by the one-body model; however, in view of the comparative importance³ of B^9 for astrophysics, direct experimental evidence would be desirable, e.g. from the reaction $\text{Be}^9 + \text{H} = \text{B}^9$

³ Bethe, "Energy Production in Stars," to appear shortly in the Phys. Rev.

$+n$ which should occur with protons of 2 Mev energy.

B^8 and N^{12} are very doubtful. B^8 is just on the limit of stability, being slightly stable according to "Calc. II," slightly unstable according to I. The stability of N^{12} depends mostly on the exact binding energy of B^{12} which is not known at present.

SEPTEMBER 15, 1938

PHYSICAL REVIEW

VOLUME 54

Bands of H_2 Ending on the $2p^1\Pi$ Level

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(Received May 5, 1938)

New measurements make possible a much more complete analysis of the band systems ending on $2p^1\Pi$. The constants of this state can be obtained with great accuracy and the irregularities in the Λ -doubling and perturbations traced to the interaction with the higher vibrational levels of $2p^1\Sigma$. New information is obtained about some of the states which have both electrons excited.

THE strongest and most extensive band systems in the visible H_2 spectrum are the transitions from a number of three quantum electronic levels to the $2p^1\Sigma$ state.¹ The data of these band systems can be found in Richardson's book² or in the original papers listed there. All the upper levels of these systems should also combine with the $2p^1\Pi$ state. The resulting band systems lie chiefly in the near infra-red around 7600Å. Important fragments of these bands have been given by Richardson and Chalk,^{2, 3} but the measurements of Gale, Monk, and Lee on which they based their analysis contain only the strongest lines in this region. Therefore it seems desirable to publish the data on these band systems as they were obtained from a more recent analysis based on our own measurements. This re-analysis was undertaken as a preliminary study for the analysis of the corresponding bands of HD and D_2 on which I hope to report in a

future paper. I am giving the results of H_2 here separately because they throw some new light on the nature of the levels with both electrons excited about the exact interpretation of which there is still a great deal of uncertainty.

The wave numbers and intensities of the transitions from the singlet $3d$ complex are given in Table I and those from the other initial states in Table II. In general it will be found that the lines which Richardson gives agree with those listed here, but there is a considerable number of discrepancies, which must be ascribed to the scantiness of the data with which Richardson had to work. A few doubtful lines are included in the tables. They are designated by a question mark. In a few bands there are undoubtedly more lines present than those given in the tables. That is indicated by the high intensity of the last listed lines. In such cases there are marked irregularities in either the initial or the final state and a prediction of the position of the line becomes too uncertain. Only when there are good combination relations can such lines be identified with any degree of certainty. In the present instances such combination relations are not always available. However there is no doubt that future research will eventually locate these lines.

¹ Whenever only one electron is excited it is sufficient to specify the state of this electron, and it is understood that the other electron is in the normal state $1s\sigma$. The full notation of the $2p^1\Sigma$ state would be $1s\sigma 2p^1\Sigma$. Only when both electrons are excited is it necessary to specify the state of both.

² O. W. Richardson, *Molecular Hydrogen and Its Spectrum* (New Haven, 1934).

³ O. W. Richardson, Proc. Roy. Soc. **A126**, 487 (1930); M. L. Chalk, Proc. Roy. Soc. **A128**, 579 (1930).

The intensities are eye estimates. Apparent irregularities in the intensities are not necessarily real, as the sensitivity of the various photographic plates may change very rapidly in this region. Quantitative intensity measurements carried out by Dr. N. Ginsburg in this laboratory are partly ready. An asterisk in the tables means that the line is a known blend.

in good agreement with Jeppesen's values (see below) except in one or two cases where there is a considerable perturbation.

All the rotational levels of the $2p^1\Pi$ state are double, and it is well known that this doubling (Λ -doubling) is due to the interaction of rotation and electronic motion. One of the components $p\Pi^-$ is uninfluenced whereas the other one $p\Pi^+$ is displaced. The magnitude of the displacement is very much influenced by the nearness of other levels with the same symmetry and the same value of J . If such levels are very close we have a typical perturbation. We know that the higher vibrational levels of $2p^1\Sigma$ overlap with the $2p^1\Pi$ state so that there is ample opportunity for the production of irregular Λ -doublings and real perturbations. Therefore it would be meaningless to calculate the constants of the $2p^1\Pi^+$ state.

The $2p\Pi^-$ levels cannot be subject to such interactions as there cannot be any Σ^- or Π^-

THE $2p^1\Pi$ STATE

The final level of our bands is also the upper level of the so-called C bands in the extreme ultraviolet of which the most accurate measurements are those of Jeppesen.⁴ From the analysis of these ultraviolet bands the constants of the $2p^1\Pi$ state are known. However, the accuracy is very considerably less than that obtainable from the visible bands. If one takes this into account the results of the present paper are found to be

⁴ C. R. Jeppesen, Phys. Rev. **44**, 165 (1933).

TABLE II. *The transitions from the doubly excited levels to $2p^1\Pi$.*

P BRANCH			Q BRANCH			R BRANCH			P BRANCH			Q BRANCH			R BRANCH			P BRANCH			Q BRANCH			R BRANCH																																																																																																																
<i>J</i>	ν	<i>I</i>	ν	<i>I</i>	ν	<i>I</i>	<i>J</i>	ν	<i>I</i>	ν	<i>I</i>	ν	<i>I</i>	<i>J</i>	ν	<i>I</i>	ν	<i>I</i>	<i>J</i>	ν	<i>I</i>	ν	<i>I</i>	ν	<i>I</i>	ν	<i>I</i>	ν	<i>I</i>	ν	<i>I</i>																																																																																																									
$^1K \rightarrow 2p^1\Pi$									$^1L \rightarrow 2p^1\Pi$									$^1O \rightarrow 2p^1\Pi$																																																																																																																						
0→0									2→2									0→0																																																																																																																						
1	12 476.79	00	12 499.43	1	12 541.61	00	1	13 286.62	2b	13 304.01	2	1	13 805.50	6	13 865.88	2	13 982.05	0	2	2	374.44	0	421.34	0	484.09*	1	2	740.91	10	861.72	1	14 027.60	1	3	3	057.16	00	152.55	00	3	874.57	0	3	674.13	7	850.00	2	4	600.81*	6	4	4	11 844.30	00d?			4			4																																																																												
1→0									$^1M \rightarrow 2p^1\Pi$									0→1																																																																																																																						
1			14 728.46	3	14 768.33	1	1			11 962.49	1d	12 013.00	00	1			11 560.25*	0	2	2	14 603.55	0	647.99	0	711.71	00	2	11 441.74	0b	560.25*	0	3	3			534.28	3d	3	807.11	1	11 975.38	0	3	3					4	326.90	00	3			13 840.60	3	13 970.01	0	4	4					4			4	644.86	2	801.70	8	4	568.30*	10																																																													
1→1									2→2									1→1																																																																																																																						
1			12 422.99	3	12 462.69	0	1			11 949.87	0	1			13 721.96	4	822.27	0	13 970.01	0	2	2	12 304.46	00	348.67	0	412.55		2	13 721.96	4	822.27	0	3	644.86	2	801.70	8	3	3			244.49*(9)		3			3	644.86	2	801.70	8	4	568.30*	10	4	4					4			4	568.30*	10																																																																					
2→1									$^1N \rightarrow 2p^1\Pi$									1→2																																																																																																																						
1			14 575.35	4	14 589.50	(6)	1			13 680.39	8	13 749.75	2	1			11 669.02	2	2	2	14 456.77	00	475.77	0	513.75	2	2			656.89	00	3	3	258.14	(6)	345.48	3	402.42	00	3	13 668.42	2	13 710.66	7	13 851.82	0	4	4	111.87	00			255.90	4	4	13 668.42	2	13 710.66	7	13 851.82	0	5	5			13 982.05* 0?		4	333.38	10	5	600.29	(10)	718.34	(10b)																																																													
2→2									1→2									2→2																																																																																																																						
1			12 403.79	3	12 418.63*	1	1			11 471.22	1r	11 508.90	1	11 578.69	00	1			13 668.42	2	13 710.66	7	13 851.82	0	2	2	12 293.22	00	310.35	0	350.22	4b	2	11 471.22	1r	11 508.90	1	11 578.69	00	2			2	600.29	(10)	718.34	(10b)						3	3			189.20	2	255.58	0	3	398.32	1	470.40	3	571.57	1	3			3	559.78	0	690.80	9						4	4	11 946.99	00	037.52	00	090.79	00	4			410.58	7			4			4	559.78	0	690.80	9						5	5			853.14	00			5			336.17	1			5			5	448.62	2	645.15	6					
$^1L \rightarrow 2p^1\Pi$									2→2									$U \rightarrow 2p^1\Pi$																																																																																																																						
1→1									2→2									1→1																																																																																																																						
1			11 821.27	4			1			13 452.76*	3	13 478.62	3	1			12 816.83	00	12 892.92	1	13 061.21	3	2	2	11 702.80	0	745.04	00	635.07	1	2	368.07	5	419.44	0	13 493.60	1	2			2	659.53	0	815.36	0	036.28	2	3	3							3	368.07	5	419.44	0	13 493.60	1	3			3	659.53	0	815.36	0	036.28	2	4	4							4	260.27	3	226.20	(9)	444.49	1	4			4			4	659.53	0	815.36	0	028.23	9	5	5							5	090.44	5	141.32	3	378.91	1	5			5			5	659.53	0	815.36	0	028.23	9								

TABLE III. Rotational differences of $2p^1\Pi^-$.
 $F(J+1) - F(J-1)$

$V=0$	UV	1	UV	2	UV	3	UV
2	302.60	302.53	286.90	287.7	271.60	271.98	256.52
3	420.36	420.68	398.49	399.35	377.14	377.96	355.41
4	534.87	536.25	507.01	509.95	479.74	481.05	453.45
4	645.44		611.67		578.71		
5	751.28		711.87		673.32		

state which might influence it anywhere near. Therefore the rotational levels of the $2p^1\Pi^-$ state should be regular and the constants calculated from them in the usual way have the theoretical meaning attributed to them in the elementary theory of band spectra. The average values of the rotational differences $F(J+1) - F(J-1)$ are given in Table III. The values in small print marked UV are those which Jeppesen derived from the ultraviolet bands. The discrepancy with our values gives an idea of the accuracy of the ultraviolet data. It is curious to see that all Jeppesen's values except one are higher than ours, which cannot be accounted for by accidental errors of measurement. The cause is probably in the somewhat roundabout way which Jeppesen had to use to extract the values in the tables from the observational data.

As usual we represent the rotational levels by the formula

$$F(J) = B_V J(J+1) - D_V J^2(J+1)^2 + \dots \quad (1)$$

and calculate the constants B_V and D_V from the first three differences in each column. For $V=3$ the data are not quite sufficient to do this. The use of more differences for the calculation of the rotational constants would not increase their accuracy as the expression (1) is a very poor approximation for all but the lowest values of J . The values obtained in this way are listed in Table IV. The values in small print are those derived by Jeppesen and from them the constants in the expression

$$B_V = B_e - \alpha(V + \frac{1}{2}) + \beta(V + \frac{1}{2})^2 \quad (2)$$

are found to be

$$B_e = 31.340, \quad \alpha = 1.626, \quad \beta = 0.022.$$

The vibrational differences between successive vibrational states with $J=1$ are given in the second column of Table V.

The rotational part in the energy level for

TABLE IV. Constants used to determine rotational levels.

V	0	1	2	3
B_V	30.532 (30.539)	28.949 (29.113)	27.411 (27.485)	25.895 (25.931)
D_V	0.0195 (0.0205)	0.0186 (0.0198)	0.0181 (0.0189)	*

* As the data are very scarce for $V=3$ the value for D_3 was obtained by extrapolation from D_0 to D_2 and then the value of B_3 calculated from the single difference given in Table III.

TABLE V. Vibrational differences of $2p^1\Pi$.

1-0	2305.51	2308.68
2-1	2171.54	2174.62
3-2	2040.25	2043.28

$J=1$ is $2B_V$.⁵ If we therefore add $2(B_V - B_{V+1})$ to the values of the second column of Table V we get the true vibrational differences which are given in the third column. From the first two differences the constants in the formula

$$\omega(V + \frac{1}{2}) - x(V + \frac{1}{2})^2 + \dots \quad (3)$$

for the vibrational energy are found to be

$$\omega = 2442.74, \quad x = 67.03.$$

The discrepancy of these values with 2468 and 88.93 which are the values which Jeppesen derived for these constants from his data is chiefly due to the different manner in which the constants were determined. Jeppesen used two more terms in formula (3). Whereas for most molecules that would give a much better approximation, for H_2 , as I have pointed out before, usually no increase in accuracy can be expected. For it is necessary to use terms with higher vibrational quantum numbers for the calculation of the constants in the more extended formula and for these the convergence of (3) which is poor even for the lowest values of V becomes so bad as to render the formula practically useless. Therefore it cannot be expected that the values of the constants derived from the more complete

⁵ In general the energy of a molecule of this type is in good approximation

$$A + B[J(J+1) - 2\Lambda^2 + L(L+1)].$$

The part $B[L(L+1) - \Lambda^2]$ which is usually omitted comes from the interaction of rotation and electronic motion (see e.g. G. H. Dieke, Phys. Rev. **47**, 661 (1935)). A is independent of J and contains the electronic and vibrational energies. For a $p\Pi$ state $L=1$ and $\Lambda=1$ and therefore the energy becomes

$$A + BJ(J+1)$$

which for $J=1$ is $A + 2B$.

TABLE VI. Λ -doublings of the $2p^1\Pi$ state.

$J \setminus V$	0	1	2	3
1	1.17	1.23	0.78	12.12
2	3.47	3.39	1.42	
3	6.51	5.93	- 3.54	
4	9.95	6.58	+27.53	
5	12.90			

formula are more accurate than those derived from just two differences, although these latter values may also be considerably different from the true ones.

Λ -DOUBLING AND PERTURBATIONS

The positions of the $2p^1\Pi^+$ levels will be influenced by the vicinity of the higher vibrational levels of $2p^1\Sigma$. Therefore we must expect irregularities in the rotational levels of $2p^1\Pi^+$. Table VI gives the Λ -doubling, i.e., $\Pi^+(J) - \Pi^-(J)$. This can be derived directly from the observations without the help of any formula, except that the relative position of one *ortho* and one *para* level must be known. We can take for this e.g., $2p^1\Pi^-(1)$ and $2p^1\Pi^-(2)$ for $V=0$. As these levels are represented well by formula (1) we can find their relative position with any desired accuracy, and this in turn will furnish all the Λ -doublings within the errors of measurement.

Figure 1 shows the vibrational levels (for $J=2$) of the $2p^1\Sigma$ and $2p^1\Pi$ states and explains the peculiarities shown by the Λ -doublings of Table VI. The vibrational levels of $2p^1\Sigma$ for $V>8$ have not been actually observed but are extrapolated values. $V=4$ of $2p^1\Pi$ was taken from Jeppesen's data.

It is well known that two rotational levels of $p\Sigma$ and $p\Pi$ with the same value of J must repel each other if they are close together. Furthermore we must remember that the spacing of successive rotational levels is much closer for $2p^1\Sigma$ than for $2p^1\Pi$. Therefore we have to pay particular attention to a $p\Pi$ -level and the $p\Sigma$ -level which lies immediately above it. Successive higher rotational levels of these two states will come closer and closer together which means that the $p\Pi^+$ levels will show more and more depression if the approach of the levels is at all close.

This is further illustrated in Fig. 2 which shows the distance between the rotational levels which perturb each other. ($V=0$ means $\Sigma_8(J)$)

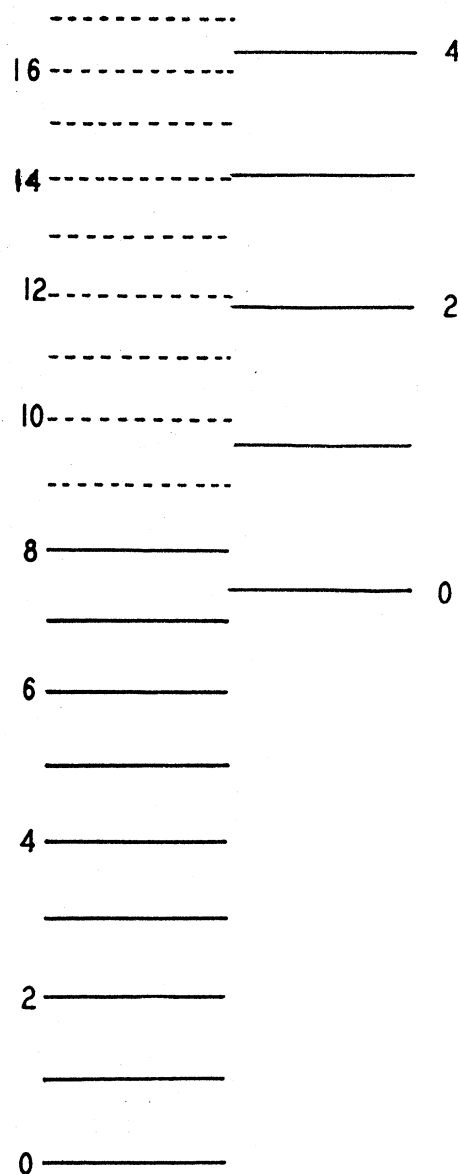


FIG. 1. Relative positions of the vibrational levels (for $J=2$) of $2p^1\Sigma$ (left) and $2p^1\Pi$ (right). The levels of $2p^1\Sigma$ with $V>8$ are extrapolated.

$-\Pi_0(J)$, $V=1$: $\Sigma_{10}(J) - \Pi_1(J)$, $V=2$: $\Sigma_{12}(J) - \Pi_2(J)$). As the $p\Sigma$ levels can be obtained only by extrapolation, the actual distances might be somewhat different from those given in the figures. The good qualitative agreement between the predicted and observed perturbations shows, however, that this difference can be only very slight. For $V=0$ and small J values the $2p^1\Pi$ levels lie practically half way between $V=7$ and

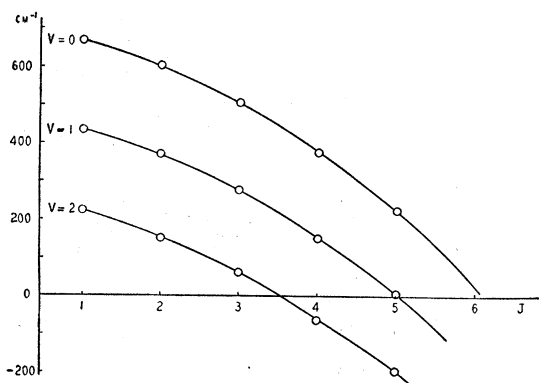


Fig. 2. Distance between the rotational levels of $2p^1\Pi$ and the closest levels of $2p^1\Sigma$ with the same J .

$V=8$ of $2p\Sigma$ and therefore the Λ -doubling shown by these levels will be very closely the normal doubling. For the highest observed J values the Λ -doubling is only slightly less than the normally expected one (which is proportional to $J(J+1)$) because the Σ_8 levels are still sufficiently far off. For $J=6$ the levels would be so close that we would have a considerable perturbation.

Figures 1 and 2 show further that the $V=1$ level of $2p\Pi$ is not very far below the $2p\Sigma_{10}$ level. For $J=1$ and 2 they are not sufficiently near to show a significant deviation from the normal Λ -doubling. However $J=3$ begins to show the influence of the nearness of the Σ_{10} levels by being appreciably depressed and $J=4$ shows this influence much stronger. $J=5$ has not been found. The extrapolated difference is only about 7 cm^{-1} which would produce a very large perturbation. It would be quite difficult to find the lines belonging to this level. $J=6$ should have an abnormally large Λ -doubling as the Σ_{10} level lies now below the Π_1 level.

This crossing over of rotational levels which gives rise to a true perturbation is actually observed for $2p\Pi_2^+$. The figure shows that this crossing over occurs between $J=3$ and $J=4$. For $J=1$ and 2 the approach is close enough so that the $2p\Pi_2^+$ levels are quite appreciably depressed. For $J=3$ the $2p\Pi_2^+$ level is so much lowered that the Λ -doubling becomes negative, whereas for $J=4$ where the Σ_{12} level lies below the Π_2 level the latter is shifted upwards and we obtain the large positive value 27.53 for the Λ -doubling.

For the Π_3 -level the situation is slightly different. Here for $J=1$ the Σ_{14} -level lies slightly

below the Π_3 -level so that the abnormally large Λ -doubling 12.12 results. For increasing J -values the Σ_{14} and Π_3 -levels grow apart. However their interaction, which is due to the influence of the rotation on the electronic motion, becomes larger with increasing rotation, so that nevertheless the Λ -doubling may remain roughly the same although J increases. Our data for $V=3$ are not quite sufficient to establish that. It explains however the fact mentioned by Jeppesen that for $V=3$ all the observed rotational levels show a perturbation of the approximately constant amount 10 cm^{-1} . There is no need to interpret this as a vibrational perturbation, as Jeppesen does. Vibrational perturbations between Σ and Π levels should be theoretically impossible.

The perturbations and the character of the Λ -doubling are thus completely explained qualitatively by the interaction of the $2p^1\Pi$ levels with the higher vibrational states of $2p^1\Sigma$. A further quantitative study would be possible if also these $2p\Sigma$ levels would be known empirically. The visible bands which come down on these levels are too weak for observation. The bands belonging to these levels in the ultraviolet $2p^1\Sigma \rightarrow 1s^1\Sigma$ system might be present but they have not been studied so far.

THE INITIAL STATES

There is no need to say much about the initial states of the bands discussed here, as they are well known from their combinations with the $2p^1\Sigma$ level which lie chiefly in the blue part of the spectrum. A few of the rotational levels of the initial states are new. In these cases their combinations with the $2p^1\Sigma$ states have been looked for and usually found.

However, a few significant facts about the states with both electrons excited came to light which deserve being mentioned. These states were first discovered by Richardson and given names 1K , 1L , 1M , 1N , 1O , 1Q . Besides there is a state which gives rise to a single progression ($\lambda 4142.8$) only (here called U). There was no place for them in the scheme of the energy levels (except possibly for 1O which was attributed by Richardson to $1s\sigma 3s\sigma^1\Sigma$) with only one of the two electrons excited, and therefore Weizel⁶ and Richardson² proposed that they must be due to

⁶ W. Weizel, Zeits. f. Physik 65, 456 (1930).

states for which both the electrons are excited. This explanation seems the only possible one also in the light of further knowledge about them.

The properties of all these states are highly irregular. We know that the interaction with other states can produce such irregularities, but if they exist it is often quite difficult to know whether a given band is genuine or spurious. In most cases the evidence which Richardson gives can leave little doubt that the bands are real, but in view of the great theoretical importance which these levels have for the knowledge of the structure of the excited hydrogen molecule, additional information about them is highly desirable.

Richardson gave also some of the transitions of K and O with $2p^1\Pi$. Table II shows that now the transitions of all these states with $2p^1\Pi$ are known with the exception of Q which was regarded as very doubtful by Richardson and not included in his book. Some of the bands are very weak and consist only of a few lines, but they are always just the lines which must be expected to be strongest. We have here thus additional independent evidence that these levels must be genuine. A few more interesting facts appear from a study of the bands in Table II.

In the transitions of the $3d$ complex with $2p^1\Pi$ as well as in the corresponding triplet bands, the bands for which the vibrational quantum number does not change are much stronger than any of the bands off the main diagonal of the vibrational scheme. According to the Franck-Condon principle such a state of affairs must be expected when the moment of inertia of the initial and final states are not much different. This argument is often reversed to find the vibrational quantum numbers from the intensity distribution of a given band system. If the bands of a given diagonal are much stronger than all the other bands it is argued that this diagonal must be the main diagonal of the system, i.e. correspond to no change in the vibrational quantum number. For the L , M and N transitions with $2p^1\Pi$ we find that with Richardson's assignment of vibrational quantum numbers the strong bands would be $0 \rightarrow 1$ and $1 \rightarrow 2$. Therefore the vibrational quantum numbers of these three states were raised by one in order to make the strong bands $1 \rightarrow 1$ and $2 \rightarrow 2$.

This procedure is not free from objections. It would imply that the moment of inertia of the L , M and N states is nearly the same as that of the $2p^1\Pi$ state, which seems highly improbable. Furthermore if the lowest known vibrational levels of these states have now $V=1$ there should be lower lying levels with $V=0$. I have looked for them but have not been able to find them. However, Richardson's original assignment of vibrational quantum numbers for these states was based on a similar argument regarding the intensity distribution in the transitions to $2p^1\Sigma$, where the state of affairs is more complex. I hope that an analysis of the corresponding D_2 and HD bands on which Miss M. Lewis is working at present will clear up the situation.

The U level has the peculiarity that for the $U \rightarrow 2p^1\Sigma$ bands only one branch in every band is known. It was impossible to decide whether this branch is a P , Q or R branch. However, the transitions from the U level to $2p^1\Pi$ show P , Q and R branches and it is seen immediately that the single branches of Richardson's 4142.8 progression must be P branches. Only one band of the $U \rightarrow 2p^1\Pi$ system is strong enough to be found, but the existence of this one is beyond any doubt. It ends on the $V=1$ level and by the same argument which was used above we conclude that the vibrational quantum number of the U level must be one. The question whether this level is a Σ , Π , Δ , etc. level cannot be decided with absolute certainty. Richardson gives the $P3$ lines in the strongest bands as the lines with the lowest rotational quantum numbers, and from that it would seem likely that U would be a Δ -state. However, the $R1$ and $Q2$ lines of the $U \rightarrow 2p^1\Pi$ band are missing, whereas the $P3$ line of this band is very weak. It is difficult to know whether the absence of these lines is significant or whether it only means that they are present but so weak that they do not register on the photographic plate. If these lines are really missing, i.e. if the $P3$ lines are spurious, the U state would have to be a Φ state.

I shall leave the discussion of possible electronic configurations for all these states to a subsequent paper.

I wish to thank Mr. W. Durdin for his help with the measurements.