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NEW FEATURES OF THE RED BAND SYSTEM OF SODIUM

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Abstract

The occurrence of an infra-red edge to the red band system of Na_2 is reported and is explained in terms of the Franck-Condon theory of intensity distribution when account is taken of the shape of the potential energy curves as dissociation is approached. The same theory explains a head of the red system in the yellow-green, the reappearance of the orange "cathode-ray fluorescence" series in the infra-red, and the observed asymmetry in the two branches of the Condon "parabola."

IN ORDER to decide a point[1] concerning the lower level vibrational terms in the red band system of Na_2 the writers have used neocyanine plates to follow this system out into the infra-red where the bands with high values of n'' occur. It was there found that the system, instead of extending indefinitely towards longer wave-lengths, as is usual, actually terminates in a fairly sharp edge at $8150A = 12300$ cm^{-1}, beyond which absorption ceases altogether. The whole situation, and in particular the contrast between the behaviors of the red and green systems is apparent in Figs. 1, 2 and 3.

Fig. 1 shows the visible absorption spectrum of sodium at various temperatures as taken with a dicyanine plate in a small glass Hilger constant deviation spectrograph. It can be seen that at low temperatures (lowest spectrum) only a few bands appear, near the origin of each system. As the temperature is raised the bands spread out, more or less symmetrically, on each side of the origins, partly because the increased density of molecules brings out the fainter bands, and partly because the increased temperature produces more molecules with high vibrational quantum numbers (n'').

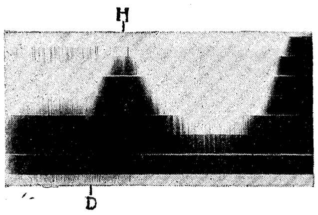

Fig. 1.

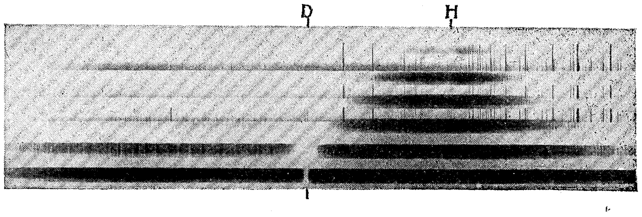

Fig. 2.

Fig. 1. Visible absorption spectrum of sodium vapor. Temperature and density increasing upward. *D* indicates *D* lines; *H* the green head of the red system. Comparison spectrum neon.

Fig. 2. Same as Fig. 1 but taken with a larger spectrograph on a panchromatic plate. Comparison spectrum iron.

Fig. 2, taken with a panchromatic plate in a larger spectrograph, shows part of the same region as Fig. 1, in greater detail.

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[1] Loomis, Phys. Rev. **31,** 328 (1928).

Fig. 3, on the same scale as Fig. 2, but taken with a neocyanine plate, shows the termination of the red system in the edge at 8150A. The lowest three spectra, which show the edge, were taken through sodium vapor so extremely dense that the transmitted light was of a deep violet color.

Fig. 3. Taken with the same spectrograph as Fig. 2, but with a neocyanine plate. Temperature and density increasing downward. *E* indicates infra-red edge. Comparison spectrum neon.

This is not a convergence limit in the usual sense since there is no continuous absorption beyond it; and since it is in entirely the wrong location to correspond to a dissociation process. The explanation of this edge and, as it turns out, of other peculiarities of this band system is to be found in an un-

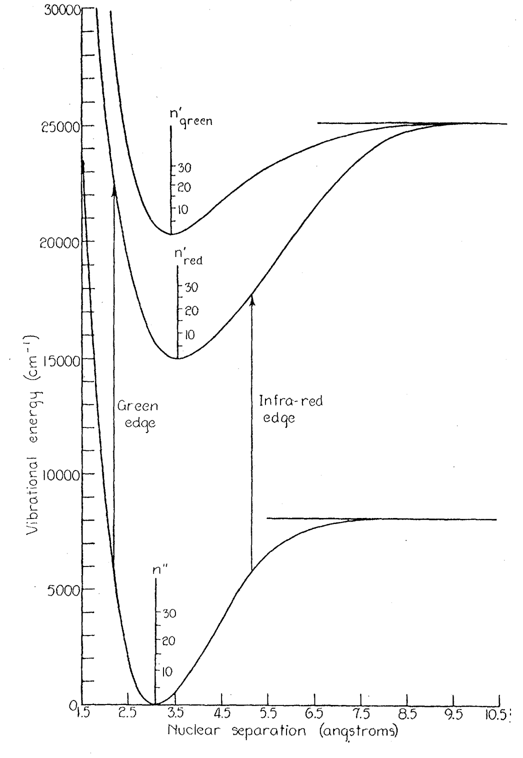

Fig. 4. Potential-energy functions of the three electronic levels.

usual distribution of intensities of vibrational transitions which in turn can be deduced according to the procedure of Franck[2] and Condon[3] from an unusual relation between the potential-energy functions in the two electronic states.

The potential-energy curves for the two electronic states which take part in the red system, as well as for the upper electronic state of the green system, are shown in Fig. 4. For convenience the electronic energy is included as potential energy. The data from which the curves were calculated are given in Table I.

TABLE I. *Constants of the molecule in three electronic states.*

State of molecule:	Normal	Upper Green	Upper Red
Electronic term:	0	20301.70[1]	15006.68[5]
$\omega_0(\text{cm}^{-1})$:	158.5[1]	124.13[1]	115.22[5]
$\omega_0 x(\text{cm}^{-1})$:	0.73[1]	0.84[1]	0.384[5]
D(volts)	1.0[1]	0.6[1]	1.25[1]
$B_0(\text{cm}^{-1})$:	0.1543[4]	0.1254[4]	0.1152
$\alpha(\text{cm}^{-1})$:	0.00082[4]	0.00094[4]	0.00043
r_0(A):	3.08[4]	3.41[4]	3.56
U_2:	+4312	+2645	+2279
U_3:	−2680	−1736	−1040
U_4:	+ 642	+ 407	+ 192

Because of the lack of a reliable analysis of the rotational structure of the red bands, no measured values of B_0' and α' are available. Those in Table I were, however, estimated, probably with greater accuracy than is here needed, by making use of the empirical relations of Mecke[6] and Birge,[7] that B_0/ω_0 and $R=2xB_0/\alpha$ are approximately constant during a transition. In the green system $B_0''/\alpha''=0.00097$ and $B_0'/\alpha'=0.00101$. Hence a plausible guess for the red system is $B_0'/\alpha'=0.00100$, yielding $B_0'(\text{red})=0.1152$. In the green system $R''=1.73$ and $R'=1.81$. An estimated $R'=1.76$ for the red system leads to $\alpha'=0.00043$. u_2, u_3 and u_4 in Table I are the coefficients of the quadratic, cubic and biquadratic terms in $(r-r_0)$ in the expression for the potential energy, calculated by Condon's formulas.[3]

Now the Franck-Condon procedure for finding the most probable vibrational transitions is to assume that they correspond to the impact of a light quantum on a molecule in which the nuclei are at rest at one or the other extreme of a vibration, and that, owing to the large nuclear mass, the transition takes place without change of r and without setting the nuclei in motion. This means that each such transition is represented by a vertical line from a point on the lower to a point on the upper curve in Fig. 4. The initial and final vibrational quantum numbers can be obtained by projecting these points horizontally onto the scales of n' and n'' and *the frequency of the light*

[2] Franck, Trans. Faraday Soc. **21,** 438 (1926).

[3] Condon, Phys. Rev. **28,** 1182–1201 (1926).

[4] Loomis and Wood, Phys. Rev. **32,** 223 (1928).

[5] Fredrickson, Phys. Rev. **31,** 1130 (1928).

[6] Mecke, Zeits. f. Physik **32,** 823–834 (1925).

[7] Birge, not yet published.

absorbed in the process is represented by the length of the vertical line. It is usual to represent the results as a graph of the values of (n', n'') associated with the most probable transitions, but for our present purpose it is preferable to plot ν against n''; or better, since n'' is less accurately known than the corresponding vibrational energy T'', to plot ν against T''.

The resulting curves for the red and green systems, based on the potential-energy curves of Fig. 4, are shown in Fig. 5. It will be seen that the theoretical curve for the red system shows a minimum frequency at 12000 cm^{-1}, which undoubtedly corresponds to the observed absorption edge at 12300 cm^{-1}, with quite satisfactory accuracy for this type of computation.

The peculiarity in the relationship between the potential-energy curves of the two molecular states which results in the infra-red edge is essentially this: Although the normal molecule is more tightly bound than the excited one in the sense that the nuclei are closer together $(r_0'' < r_0')$ and the frequency of vibration is greater $(\omega_0'' > \omega_0')$, it is at the same time less tightly bound in the sense that the energy required to dissociate it is less $(D'' < D')$. This unusual relationship has as a consequence that the potential energy curve of the excited molecule is flatter near the minimum and also has its minimum further out than that of the normal level, but that it eventually rises higher. The result is that the frequency of the light absorbed during the transition, represented by the length of the vertical line joining the two potential-energy curves, at first decreases with increasing r, but that eventually it must increase again and that there is therefore a minimum at about the point where the vertical arrow is drawn in Fig. 4. It should be noted that while the location of this minimum frequency depends on the estimated constants of the upper state, its existence follows necessarily from the fact that $\omega_0'' > \omega_0'$ while $D'' < D'$.

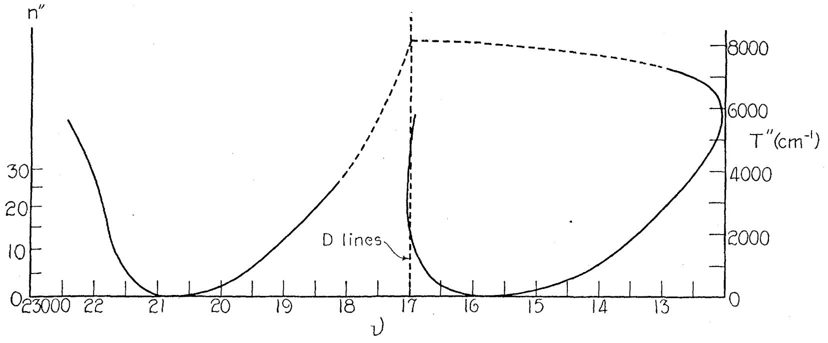

Fig. 5. Calculated locus of most probable vibrational transitions for each vibrational quantum state, n'' (scale at left) or for each amount of vibrational thermal energy, T'' (scale at right).

Fig. 5 also affords an explanation of the curious appearance of the yellow-green region in the absorption spectrum of very dense sodium vapor. It can be seen in Fig. 1 that as the vapor density is raised the red system expands across the D lines and appears to come to a head at about 5500A = 18200

cm^{-1}, in a region of very strong absorption, which is indicated by H in Figs. 1 and 2. The region of just shorter wave-length than this is comparatively transparent, though not completely so. At still shorter wave-lengths the green system shows up strongly, so that there is a narrow transparent region which sometimes looks rather like an emission band. In Fig. 5 it appears that the curve of most probable transitions for the red system has a maximum frequency at 17000 cm^{-1}. This almost certainly corresponds to the observed head at 18200 cm^{-1}, the large error being due to the necessity of using the steep parts of the potential-energy curves in the calculation. The green system certainly extends across this region, to convergence at the D lines, but the bands which occur here are due to molecules with such high vibrational energy that they are rather rare at these temperatures, and the bands rather weak. Hence the comparative, but not complete, transparency just short of 5500A.

A further characteristic of the bands of the red system can be deduced from the character of the potential-energy curves, as follows: As is apparent in Fig. 4, the potential-energy curve of the normal molecule rises more rapidly at first than that of the excited molecule ($r_0'' < r_0'$ and $\omega_0'' > \omega_0'$) but does not have to rise so high ($D'' < D'$); hence it becomes sensibly horizontal at a much smaller value of r. For instance, according to Fig. 4 the lower level molecule is nearly dissociated at 6A, where the upper one has only about half the necessary energy. Hence the vibrational levels of the lower electronic level are here crowded closely together, while those of the upper electronic level are still well separated. Hence $\omega'' < \omega'$ in this region. Consequently, by Mecke's rule, $B'' < B'$ and the bands must degrade to the violet. That is, although the bands near the system origin are sharply degraded to the red, and have their heads on their R branches, very close to their origins, the heads must finally move away to infinity and eventually reappear on the other side, on the P branches.

This is a little surprising, because a simple calculation based on the constants of Table I, shows that as long as a linear representation of B as a function of n will suffice, the displacement of band heads from their origins is quite insignificant. Indeed this displacement, $\nu_0 - \nu_H = B'B''/(B' - B'')$, amounts to only 0.46 cm^{-1} at the origin of the system, and the variation of this quantity,

$$\delta(\nu_0 - \nu_{\mathrm{H}}) = \left(\frac{B''}{B' - B''}\right)^2 \alpha'\delta n' - \left(\frac{B'}{B' - B''}\right)^2 \alpha''\delta n''$$

would not in any case amount to more than a few tenths of a cm^{-1}. One is forced to conclude that the linear representation of B becomes *completely* inadequate as dissociation is approached.

It may well be that the changing structure of the bands as one proceeds towards the infra-red accounts for the discrepany reported by Frederickson,[5] between the absorption heads and the magnetic rotation lines. The magnetic rotation lines to which vibrational quantum numbers can be assigned coincide, according to theory,[1] with the R branch heads only, since Q branch lines should not produce rotation. In the case of bands near the system origin, measurements of absorption heads will also be made at the head of the R branch, since this will be stronger than the head of the Q branch and will stand out at the edge of the band. But as one proceeds into the infra-red the appearance of the bands will change and the lines of the Q branch will pile up on each other so that it will be natural to measure them as the absorption head. In this case there will be a discrepancy between magnetic rotation and absorption measurements.

The series of bands in the orange found by Wood and Galt[8] in the cathode-ray fluorescence of sodium vapor has been interpreted by Schüler[9] as belonging to the red band system. The spacing between successive bands of this series is approximately that of the lower vibrational levels. Sodium molecules are presumably excited by collisions of the second kind with excited sodium atoms, which give the molecules 2.1 volts energy and leave them in the upper level of the red system and with a very limited range of values of n' and j'. These molecules then return to the various vibrational levels of the lower electronic level and in the process emit the series of bands, very much as in fluorescence. The occurrence of a few bands of higher frequency than that of the D lines is accounted for in the same way as anti-Stokes lines in fluorescence, by the molecules which happened to possess one or more vibrational quanta before they were excited. On this interpretation the series of bands in the orange, which was reported by Wood and Galt, correspond to transitions in which the molecule returns to a comparatively low value of n'', and they would be represented on the usual Franck-Condon diagram, by a horizontal row of points at the value of n' which the 2.1 volts happen to excite and *lying on, or near, the left arm of the Condon parabola.* It is expected however that transitions will also take place to much higher values of n'', corresponding to the right arm of the parabola; and indeed that the transitions to the right arm will be greatly preferred over those to the left arm, for a reason which will be discussed below. The results of the present paper make it clear that the wave-length of the bands corresponding to the right arm of the parabola in this cathode-ray series should be in the neighborhood of 8000A not far short of the infra-red edge. This was verified when the cathode-ray fluorescence was rephotographed with a neocyanine plate,[10] and it was found that the series actually do recur in this region.

A point which seemed to stand in the way of the above interpretation of the cathode-ray fluorescence spectrum has recently been cleared up in a discussion with Professor J. Franck. The difficulty was that Wood and Galt published a spectrum in which the series of cathode-ray fluorescence bands appear to be reversed. Now the processes which give rise to the cathode-ray fluorescence series may be symbolized by

$$A'+M(n_0'')=A+M(n')=A+M(n_1'')+h\nu$$

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[8] Wood and Galt, Astrophys. J. **33**, 72–80 (1911).

[9] Schüler, Zeits. f. Physik **43**, 474–479 (1927).

[10] Wood and Loomis, not yet published.

which indicates that in the first stage an excited atom A' gives up its energy to a molecule in the normal electronic level with n_0'' vibrational quanta, thereby becoming a normal atom A and raising the molecule to the upper electronic level with n' vibrational quanta. In the second stage the molecule emits the quantum $h\nu$ and returns to the lower electronic state with an altered number n'' of vibrational quanta. If these processes were reversed in a single step, as the apparent reversal of the spectrum seems to indicate, it would imply that the quantum which was absorbed divided its energy between exciting an atom and adding a few vibrational quanta to a molecule. If the possibility of this sort of three-body collision between a quantum, an atom and a molecule is admitted, it becomes difficult to account for the absence of this series in absorption in ordinary sodium vapor. The correct explanation which, although complicated, seems to correspond to the experimental conditions under which the spectrum is found, is probably as follows. It occurs on the background of "white-light fluorescence" of sodium vapor. The white light excites a very broad (say 50A) atomic D line fluorescence. This very broad D line becomes reversed in travelling over to the field of view of the spectroscope. It there excites a fluorescence series in the red band system and in this series the pattern of the reversed D line is repeated at intervals of ω'' from the exciting D lines. In the resulting spectrum the broad emission lines merge into an apparently continuous background, on which the reversed center recurs at intervals and appears to be an absorption series.

It appears to be a general feature of the intensity distribution cases where the Condon parabola is as wide open as this, that the right arm of the parabola is in reality much stronger than the left. In other words it is much more probable that a molecule with a given high value of n' will revert to a high than to a low value of n''. This effect is masked in absorption by the opposing effect of the Boltzmann factor, so that the two arms of the parabola appear about equally strong. It is however very marked in fluorescence series. In a detailed study by one of us of all the sodium fluorescence series reported by Wood, it was found that in every case where the absorbing line belonged to a band on the left arm of the Condon parabola the fluorescence series extended over to the right arm; but in most cases where the absorbing line belonged to the right arm the fluorescence series did not extend back to the left arm. The same asymmetry in the transition probabilities corresponding to the two arms is clearly apparent in Wood's experiments with fluorescence excited in sodium vapor by light of varying frequency from a monochromator. The explanation of this asymmetry is, in terms of the Franck-Condon theory quite simple. When n' is high the amplitude of vibration is large and the vibration extends well up onto the lip, or flat part, of the potential-energy curve. The molecule then spends a greater proportional part of its time on this part of the curve, i.e., with nuclei far apart and is more likely to emit the quantum when in this state. Transitions made when the nuclei are most widely separated correspond to the right arm of the parabola, and this arm is therefore more prominent, particularly for large values of n'.

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Fig. 3. Taken with the same spectrograph as Fig. 2, but with a neocyanine plate. Temperature and density increasing downward. *E* indicates infra-red edge. Comparison spectrum neon.

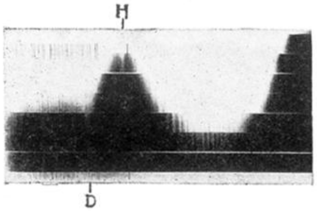
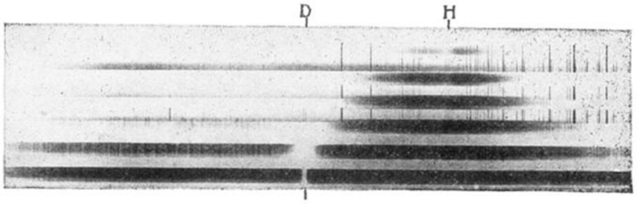


Fig. 1.



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