JUNE 1, 1931 PHYSICAL REVIEW VOLUME 37

REPULSIVE ENERGY LEVELS IN BAND SPECTRA

By Joseph Kaplan
University of California at Los Angeles

(Received April 20, 1931)

Abstract

An explanation is given for many cases of anomalous intensity distribution in the band spectra of diatomic molecules. Use is made of an interaction between the known energy levels of molecules and energy levels which are produced by the repulsive interaction of pairs of atoms in their normal and metastable energy levels. The chief types of anomalies which are discussed are those corresponding to the sudden cutting off of a group of bands at some low value of v', the initial vibrational quantum number, and the failure of bands to agree with the Franck-Condon theory. Use is made of these ideas to explain the long life of active nitrogen.

While there have been some very unusual cases of intensity distribution in the band spectra of diatomic molecules, they have been the exception rather than the rule and for that reason very little attention has been paid to them. The writer has made use of some of these cases to calculate the heats of dissociation of nitrogen[1] and of carbon monoxide[2] and until recently nothing more was done with them. Recent experiments on some very unusual band spectrum intensites in nitrogen-oxygen mixtures, combined with the increased interest in the purely repulsive potential energy levels of Heitler and London,[3] have led the writer to what is believed to be a satisfactory explanation of many of the unusual examples of band spectrum excitation which have arisen. The recent paper by Turner[4] on the effect of magnetic fields on the fluorescence radiation of iodine, suggested the direction in which an explanation was to be sought for the above-mentioned cases. In this note we will only mention these cases and make brief remarks about their explanations.

As a typical example we will consider the second positive group of nitrogen. These bands correspond to transitions from the C level to the B level. No bands of this system are known whose initial levels are higher than $v'=4$, in spite of the fact that the total energy of the "C" level is about 15 volts, corresponding to dissociation into a ^2D and a ^2P metastable atom.[5] The energy in the C_4 level is about 13.9 volts and this is exactly equal to the dissociation energy of nitrogen into two metastable ^2D atoms. Therefore, unless the products of dissociation are assumed to be two ^2D atoms rather than a ^2D and a ^2P atom, one cannot explain the non-appearance of the higher vibrational levels by saying the $v'=4$ is the highest vibrational quantum number that

---

[1] J. Kaplan, Proc. Nat. Acad. Sci. **15**, 226 (1929).
[2] J. Kaplan, Phys. Rev. **35**, 957 (1930).
[3] Heitler and London, Zeits. f. Physik **44**, 455 (1927).
[4] L. A. Turner, Zeits. f. Physik **65**, 464 (1930).
[5] Mulliken, Phys. Rev. **32**, 186 (1928).

can be associated with the C level. An alternative explanation presents itself if one assumes that all vibrational states above $v'=4$ are quenched by transitions from the C level to the Heitler and London level which corresponds to the coming together of two metastable ^2D atoms. The probability of transitions from the stable molecular level to a Heitler and London level is undoubtedly governed by the same rules as those which govern the usual molecular transitions e.g. by the Franck-Condon principle. Thus one can in general study the shape of the potential energy curve corresponding to a Heitler and London level, from the way it combines with known potential energy curves. The writer proposes to make a careful study of this in the future.

There are two possible explanations for the case which was just discussed, so that we propose now to discuss some more convincing examples of interaction between repulsive and attractive potential energy curves. The fourth positive bands of nitrogen are developed with but one initial vibrational state, corresponding to the transition D_0-B_v. The writer has used this fact as a means of calculating the heat of dissociation of nitrogen, making the postulate that the reason for the non-appearance of higher vibrational states was that the molecule spontaneously dissociated when an attempt was made to excite the higher vibrational states. At the time the calculation was made this was thought to indicate an extreme anharmonicity of the D level and consequently a very small heat of dissociation for this level. The value of $\omega_0 x$ necessary to yield the extremely small value of D^v that this explanation demanded was so large as to be without precedent among band spectra. The present explanation will be seen to be much more reasonable. A purely repulsive potential energy curve corresponding to the coming together of a ^2D and a ^2P atom would cross the potential energy curve of the D level at just about the energy corresponding to its first or second vibrational states. Even if the D level does possess some vibrational states, a strong intercombination with the Heitler and London level might either prevent the excitation of these higher vibrational states or if they were excited, it might quench them. Probably both of these effects must be considered, but once again it is seen that a Heitler and London level is useful in explaining an unusual spectroscopic phenomenon.

Similar considerations may be applied to the third positive group, the $3A$ bands and the $5B$ bands of carbon monoxide.[6] All three of these groups possess but one initial vibrational level and the writer has used the lowest one of these electronic levels, the b level, as a means of calculating the heat of dissociation of CO, making the same assumption as was made for the D level in nitrogen. The generally accepted value for the heat of dissociation of CO is around 10.3 volts and the energy values of the initial levels of the third positive and the $5B$ bands are 10.34 and 10.61 volts respectively. Thus it is gain highly probable that the repulsive energy level which corresponds to the coming together of a normal carbon atom and a normal oxygen atom, will so combine with these two electronic levels as to prevent the excitation of higher

---

[6] J. Kaplan, Phys. Rev. **36**, 784 (1930).

vibrational states. The repulsive interaction of a normal oxygen atom and a carbon atom in the ${}^1S_0$ state will yield an energy level in the vicinity of 11.5 volts, and this will account for the absence of vibrational states higher than $v'=0$ in the $3A$ bands of CO.

Returning to the consideration of the nitrogen molecule we call attention to several other cases of anomalous intensity distribution in band spectra, which seem to be examples of interaction between attractive and repulsive levels in the molecule. A system of nitrogen bands, discovered by Birge and Hopfield,[7] and having but a single initial vibrational state at 12.8 volts, shows a very unusual intensity distribution among the bands of the progression. Now 12.8 volts corresponds very closely to the energy of recombination of a normal nitrogen atom and a metastable atom in the ${}^2P$ level. Once again therefore we can blame the peculiar development of the bands on an interaction between an attractive and a repulsive energy state. In the same report, Birge and Hopfield call attention to many irregularities in the bands which make up the ultraviolet system ${}^1S-{}^1P$. Since the electronic energy of this system is 8.5 volts and most of the irregularities are connected with the progressions arising on $v'=4$, 5 and 6, the explanation is given that these irregularities arise from interactions between this level and the repulsive level which is formed when two normal nitrogen atoms come together. The heat of dissociation of nitrogen is about 9.1 volts[8] and the energy of the $v'=4$ level is 9.3 volts. By comparison with the previous examples it is certainly reasonable to assume that the above explanation is correct.

The experiments which first called the writer's attention to the possibilities of the ideas presented here, were designed to reproduce some of the peculiar intensity phenomena which arise in the first positive bands of nitrogen as produced in the aurora borealis. Without attempting a detailed discussion of the experiment, we can say that as far as the intensity distribution among the bands is concerned, especially when the relative intensities of the bands in a single v' progression are considered, the first positive bands are surprisingly sensitive to excitation conditions, more so in fact than any other band system with which the writer has had experience. Elsewhere[9] the present writer has called attention to the violent variation in intensities which arises when inert gases are mixed with active nitrogen. This variation in intensities, which is a variation of intensities in v' progressions, must be looked on as a variation in transition probabilities, because the relative intensities of bands within a v' progression are fixed by the relative transition probabilities, which can be determined by the Franck-Condon principle. In practically all discussions of band spectra it is assumed that the predictions of the above principle hold and in general they do apply. The anomalous cases presented here are those which arise either under unusual excitation conditions or in the case of energy levels which are very sensitive to excitation conditions and thus yield exceptional intensities even under normal dis-

[7] Birge and Hopfield, Astrophys. J. **68** 257 (1928).

[8] Birge, Trans. Faraday Soc. **25** 718 (1929).

[9] J. Kaplan, Phys. Rev. **36,** 778 (1930).

charge conditions. A few more remarks about the first positive bands will soon convince us that it is partly an example of the very sensitive energy state rather than that of unusual excitation conditions.

It is easy to see, from only a casual inspection of the spectrum, some of the unusual features of the first positive bands. One unusual feature is, that while most of the first positive bands possess four heads, the bands whose initial levels correspond to $v'=13$, 14, 15, 16 and sometimes $v'=17$, as well as those with $v'=19$, 20, 21, possess only strong single heads. In some discharges even $v'=3$, 4 and 5 showed this characteristic. Under some conditions there are remarkable variations in the relative intensities of the four heads and sometimes only one strong head appears where four appeared under normal conditions. Furthermore the intensities of the bands which possess these single-heads under normal conditions, are less than those originating on higher vibrational states, which is in itself an exceptional occurrence, and in agreement with the idea that the vibrational states corresponding to the single-headed bands are quenched by some mechanism in the molecule. In some of the experiments on the spectra of oxygen-nitrogen mixtures it was possible to produce the first positive bands with a sharp cut-off at $v'=12$. The vibrational states higher than $v'=12$ were almost completely missing thus giving here an excitation similar to some of the examples discussed above for NO, N_2 and CO.

A calculation of the energies corresponding to the range of vibrational states from which single-headed bands arise shows them to be in regions of the potential energy curve where one might quite reasonably postulate interaction with repulsive energy levels of the molecule. The vibrational levels associated with the initial electronic state of the first positive group lie between 9.35 and 13.9 volts. In this range there are four possible Heitler and London levels corresponding to the coming together of two normal atoms, or one normal and one ^2D metastable atom or one normal and one ^2P atom or two ^2D atoms. We therefore readily see why this group of bands should be so highly sensitive to changes in conditions of excitation. The energies of recombination corresponding to the above modes of interaction are 9.1, 11.47, 12.66 and 13.84 volts. The observation in some experiments of single headedness around $v'=3$ probably corresponds to the 9.1 volt level, the $v'=13$ to 17 correspond to both 11.47 and 12.66 since their energies lie just between these two values and finally the single headed bands around $v'=20$ or 21 can correspond to either 12.66 or 13.84.

The most interesting application of the idea of interaction between attractive and repulsive levels is to the problem of the afterglow of active nitrogen. Here the question has often been asked as to the reason why the afterglow persists for such a long time. What is the mechanism in the nitrogen molecule which regenerates metastable atoms, normal atoms and metastable molecules and keeps the afterglow visible for what is a very long time when one considers the degree of metastability of the energy states involved. If we postulate that many of the molecules in the initial states of the first positive bands interact with Heitler and London levels and dissociate instead of radiating, then we have a direct mechanism for sustaining the afterglow. We literally allow the molecule to waste its time during the process of the decay of the afterglow. It may be that only a very small number of excited nitrogen molecules lose their energy by radiation, most of them simply redissociating due to interaction with one of the repulsive levels. Thus if the walls of the afterglow tube are such as to allow the persistence of atoms, and it is well known that the walls are of paramount importance here, then one can expect a very long duration for the glow. Until further investigation has been made, it is not possible to say which of the two factors governs the life of the glow. It will be an interesting problem to study the effect of this new factor on the life of the nitrogen afterglow.

One final example will be discussed because of the good numerical agreement with heats of dissociation to which it leads. It has been known for a long time to spectroscopists that the beta bands of nitric oxide possess a very exceptional intensity distribution.[10] These bands were first discovered in active nitrogen and the intensity distribution to which we refer is the one which is observed there. The writer has reported two experiments in which the beta bands were observed in the discharge but no careful study of intensity distribution has been made there. The two main anomalies in the intensity distribution in active nitrogen are the failure of the bands to fit the Franck-Condon theory and the absence of progressions higher than $v'=4$ even though $v'=5$ has been observed in absorption. The energy of the $v'=4$ level of the B band system is 6.15 volts and about three years ago the writer made some calculations of heats of dissociation of N_2 and O_2, using this as the heat of dissociation of NO. The success of this method in N_2 and CO was the reason for these calculations. The resulting value for O_2 was so low that it was not considered at the time. In view of the recent revisions of the heats of dissociation of N_2 and O_2, it is now possible to calculate a new value for NO,[11] using 9.1 volts for N_2 and 5.06 volts for O_2. The heat of dissociation of NO is found to be 6.15 volts so that the explanation is immediately apparent. We have here an example exactly like that of the second positive bands of nitrogen. The fact that in this case the phenomenon is observed in active nitrogen, where the interaction between attractive and repulsive levels is probably rather strong, makes the explanation more interesting. Here again we postulate an interaction between the excited states on which the beta bands arise and the Heitler and London level corresponding to the coming together of a normal oxygen and a normal nitrogen atom. The failure of the beta bands to obey the Franck-Condon rule for band intensities is added evidence that the proposed explanation is correct, since that also occurred in some other cases mentioned earlier in this paper.

We have seen that the interaction between a repulsive and an attractive level will account for the sudden curtailing of band systems and that many such examples are accompanied by a failure of the bands to obey the Franck-Condon rule. This latter phenomenon can be referred to as a variation of

---

[10] Barton, Jenkins and Mulliken, Phys. Rev. **30**, 175 (1927).

[11] Birge and Sponer, Phys. Rev. **28**, 259 (1926).

intensity within a progression, because a little consideration will show that the Franck-Condon rule predicts very definitely only the relative intensities within a single progression. Without going into much detail at this time it can be shown how the interactions which account for the curtailing of band systems will also account for a variation of intensities within a progression. The Franck-Condon theory is usually applied in a qualitative manner by drawing the two potential energy curves which are involved and noticing what lower states result when vertical lines are drawn through the two extreme values for the separation of the two atoms in the vibrating molecule. This procedure is correct provided the initial state radiates to, or in any other way goes to, only a single lower electronic state. The relative intensities of the bands which arise on a single initial vibrational state are then definitely fixed. If however the upper state finds itself in a position to interact with another lower state, the transition probabilities can be fixed now only by a consideration of both lower potential energy curves. It is obvious that one might readily expect large variations in the intensity distribution in progressions in this way. In the present paper we have shown how a third lower level, namely the Heitler and London level, may be brought in to the picture. From the nature of the observations it appears that this third level is sensitive to conditions and thus the intensity of interaction with normal levels will vary a great deal.

The present paper has been written mainly to bring out the one idea which is presented here. For that reason we have not published any spectra. This will be done in other publications which can be brought out with more leisure and in more detail, since this work is now being extended.