[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Second Order x Bands in Absorption Spectra

BY GILBERT N. LEWIS AND JACOB BIGELEISEN

Every molecule that absorbs light has a major axis, x axis, the direction of which can often be foretold from the shape and character of the molecule. Thus in a very long, conjugated molecule the x axis will be more or less along the line of maximum extension. In the quasi-classical theory of Lewis and Calvin[1] excitation by light produces an oscillation of the electron cloud along the axis. This may be regarded as a (quantized) alternating current along the axis. A higher excitation results in a second oscillation[1a] of greater amplitude.

It was assumed by Lewis and Calvin that the whole system of mobile electrons, moving in unison according to quantum rules, could be replaced in thought by a single oscillator, so that the electronic oscillations might be regarded as analogous to the vibrations of a diatomic molecule. Thus we may construct a potential diagram as for example in Fig. 1, where a constant b times the potential V is plotted vertically, and horizontally the displacement of what may be considered as the center of gravity of the electronic cloud. Let us represent the energy of the ground state by the line marked 0 and that of the first excited state by the line marked 1. The difference in these energies corresponds to the main electronic absorption band of the molecule. If the energy of the second excited state is indicated by the line 2, then by our analogy, if we are in that part of the potential curve that is parabolic, that is, if the oscillator is harmonic, twice the difference in energy $0 - 1$ would be equal to the difference $0 - 2$ but the probability of the $0 - 2$ jump would be zero. In other words, the second order x band would be an "octave" of the first, but of zero intensity. If, however, the second excitation falls in a region of anharmonicity, such as shown between the lines s and r, the upper energy levels will be closer; and the frequency, $\bar{\nu}'$, of the second order, or x' band, will be less than twice the frequency, $\bar{\nu}$, of the x band; while the relative intensities of absorption, ϵ'/ϵ, will increase as $\bar{\nu}'/\bar{\nu}$ diminishes.

In the absorption spectra which had been obtained for the polyenes and the carotenoids Lewis and Calvin[1] found a set of bands that conformed to the above conditions and which they concluded to be the x' bands. Since, however, the second order bands of these substances were at high frequencies, where they might be confused with other bands ("partials"), it has seemed desirable to look for x' bands in cases where the x band is in the red or infra-red. Unfortunately, the literature furnished few suitable spectrograms, but a considerable number have now been obtained in this Laboratory.

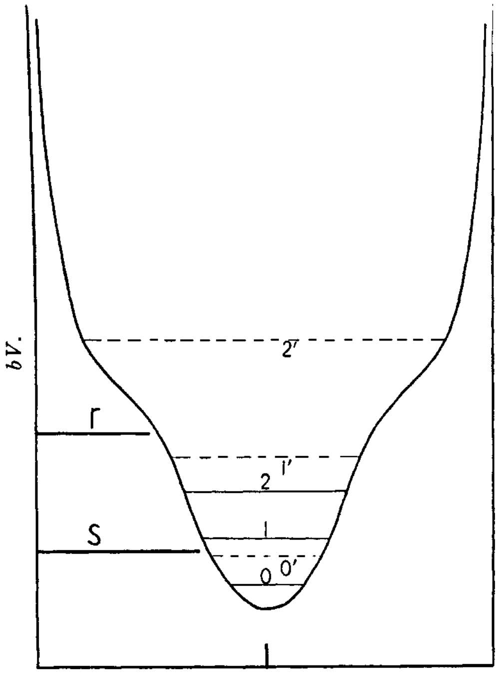

Fig. 1.—Potential curve for electronic displacements in dye molecules that have left and right symmetry.

As examples of long molecules we have chosen cyanine, 3,3'-diethylthiatricarbocyanine[2] and xenocyanine. For furnishing us samples of the last two we are deeply indebted to Dr. L. G. S. Brooker and the Eastman Kodak Co. Our extinction data are given in Figs. 2, 3 and 4. In each case we see a weak second band at something less than twice the frequency of the main band. The ratios of frequencies and of extinctions of the two bands are given in Table I.

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[1] Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).

[1a] We regard these quantized oscillations as coming within the scope of the ordinary resonance formulas used by chemists. In other words, in a molecule containing an even number of electrons, the electrons remain paired in the excited as well as in the normal state. There are doubtless cases of "forbidden" excitations to states that are not in the same class as the ground state—for example, having a different multiplicity—but such transitions are not found in the ordinary spectra of dyes. It may be pointed out that in the ground state there are electronic motions, corresponding to the zero point energy of the system, but these motions are random and without regard to the optical axes of the molecule. But in the excited molecule the oscillations have a definite direction, along the x or the y axis.

[2] The curves of Brooker, Sprague, Smyth and Lewis, THIS JOURNAL, **62**, 1116 (1940), and of Fisher and Hamer, *Proc. Roy. Soc.* (London) **A154**, 715 (1936), were not continued to quite high enough frequency to show the x' bands. Dr. Brooker informs us that a later curve of theirs for the thia compound, agreeing with ours, was published by Sklar (*J. Chem. Phys.*, **10**, 526 (1942)), but the 24,400 cm.$^{-1}$ was obscured in the drawing.

TABLE I

	$\bar{\nu}$, cm.$^{-1}$	$\bar{\nu}'$, cm.$^{-1}$	$\bar{\nu}'/\bar{\nu}$	ϵ'/ϵ
Cyanine	16800	29500	1.76	0.049
3,3'-Diethylthiatricarbocyanine	13150	24400	1.85	0.032
Xenocyanine	10700	20000	1.86	0.060

In the first two ϵ'/ϵ diminishes as $\bar{\nu}'/\bar{\nu}$ increases, as we expect for a slightly anharmonic oscillator of the type illustrated by that part of Fig. 1 below r. The large value of ϵ'/ϵ for xenocyanine cannot be interpreted without using the whole of the potential curve, as we shall do presently.

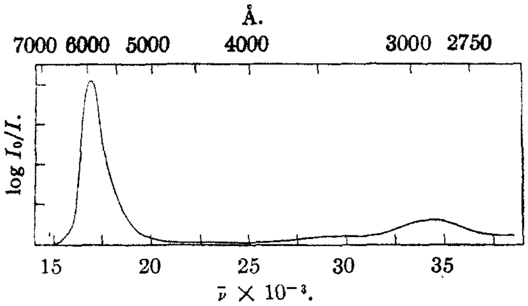

Fig. 2.—The absorption spectrum of cyanine in ethanol at room temperature.

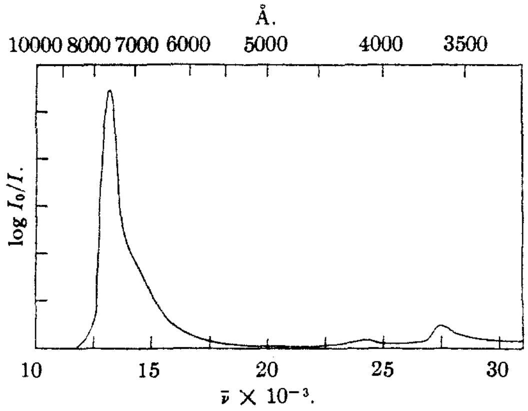

Fig. 3.—The absorption spectrum of 3,3'-diethylthiatricarbocyanine in ethanol at room temperature.

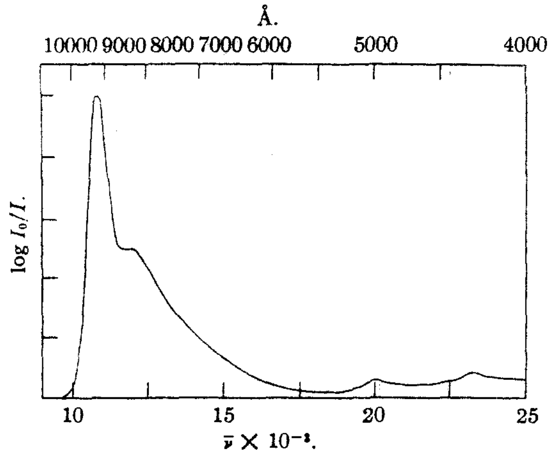

Fig. 4.—The absorption spectrum of xenocyanine in methanol at room temperature.

We have not as yet attempted to interpret the third prominent band of each spectrum and shall not attempt to until we learn more concerning the y bands and the bands of "partial" oscillation.[1] In fact we have given no positive proof that these second bands are x' bands. Such proof will rest on orientation experiments with polarized light.

We cannot hope to find for any substance so far investigated the third order or x'' band. If, however, we could study a very long molecule of good resonance with absorption between 15,000 and 20,000 Å., there might be a hope of finding the third order bands.

We shall next consider the odd ions produced by chemical or photo-oxidation. It is in these cases that we were able to show conclusively[3] that both of the two electronic band groups belong to the x system.

The ion of Wurster's blue is stable enough to study in an aqueous solution of the proper pH, at room temperature. We have studied its spectrum over a wide range and find, in addition to the highly resolved x band with its first maximum at 16,400 cm.$^{-1}$, considerable absorption in the near ultraviolet with a strong maximum at 30,500 cm.$^{-1}$ which is 1.86 times the first x frequency. However, the spectrum is hard to interpret since it seems that the y and x' bands occur in the same region.

In the more interesting case of the benzidines, the ions are unfortunately unstable at room temperature and we therefore had to use the spectrophotometer which reads only between 3600 and 8100 Å. Each of the ions of the three substances benzidine, tetramethylbenzidine and *sym*-diphenylbenzidine have well resolved x and x' band systems. But when the whole x system is within the field of measurement, the x' system is nearly out of it, and *vice versa*. The ion of benzidine itself has three vibrational bands of the x system, the one of highest frequency at 14,300 cm.$^{-1}$, the next at 12,800 cm.$^{-1}$, and the maximum of the next beyond the limits of observation. But the trend of the curve is such as to indicate the same wave number difference as between the other two, which would bring the farthest infra-red maximum to 11,300 cm.$^{-1}$.

In tetramethylbenzidine the two highest vibrational bands are at 12,700 and 14,100 cm.$^{-1}$ with almost the same difference as in the benzidine ion. Again we may extrapolate and find for the vibrational band farthest in the infra-red, 11,250 cm.$^{-1}$.

In the case of diphenylbenzidine only a part of the last vibrational band comes within the experimental field. But assuming this curve to be the same as the others, except for a displacement toward lower frequency, we may make a rough extrapolation and predict for this substance a band

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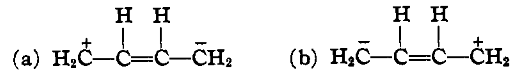
(3) Lewis and Bigeleisen, THIS JOURNAL, 65, 520 (1943).

of lowest frequency in the nieghborhood of 10,000 cm.$^{-1}$ (10,000 Å.). In this case the second order x system has been carefully examined and the first vibrational x' band is at 20,000 cm.$^{-1}$. Dividing this by the extrapolated frequency 10,000 cm.$^{-1}$ of the corresponding x band we find $\bar{\nu}'/\bar{\nu}$ approximately 2, a value that can lay no claim to accuracy. Nevertheless, we are going to see now that we are to expect and that we actually find cases in which $\bar{\nu}'/\bar{\nu} > 2$.

The Complete Potential Curve.—In nearly all, if not all, of the cases discussed so far, the energy of the molecule excited by x' absorption may be considered to lie in the region between the lines s and r of Fig. 1. In this region the energy increases less rapidly than the square of the displacement, x. This, however, cannot continue long. We know that in the first excited state the relative position of atoms is very nearly the same as in the ground state. This presumably is true of the second excited state also. Thus the electronic oscillations must occur within a nearly fixed framework of atoms.

We are accustomed to write limiting resonance structures, for example for a polyene



(a) $\mathrm{H_2\overset{+}{C}-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-\overset{-}{C}H_2}$ (b) $\mathrm{H_2\overset{-}{C}-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-\overset{+}{C}H_2}$

That such formulas represent practically the limit of electronic displacement is seen when we recognize that the right-hand carbon of formula (a) has its full complement of eight electrons, and any further electronic addition would be contrary to the Pauli principle, unless the added electrons should take positions of very high energy, in the shell outside the main valence shell. Therefore it is evident that our full potential curve must be of the form shown in Fig. 1, where, as we approach the displacement represented by the vertical lines, and corresponding to the limiting resonance formulas, the potential increases very rapidly with increasing x. In this region the separation of two successive excited levels will be greater than that shown in the lower part of the diagram. Consider a series of similar substances in which the second excited level rises progressively from a position below s to one well above r, the several levels being now indicated by the dotted lines 0′, 1′ and 2′. Then we expect $\bar{\nu}'/\bar{\nu}$ to begin nearly at 2, to fall, then rise again and finally pass through and exceed 2. If it should happen to be just 2, it would not indicate an harmonic oscillator, nor would it mean that ϵ'/ϵ should be small.

On account of the variability in the parameter b, it is not implied that when a potential curve of the same form is used for a number of substances, the energy levels are actually higher in cases where they appear in the upper part of the diagram. We shall see that the opposite is true. The only thing that determines what part of the potential curve is concerned is the amplitude of the electric oscillations relative to the dimensions of the molecule. In a long molecule such as that of β-carotene, with a first absorption band at about 4800 Å., the amplitude of the electronic oscillations in the first and even in the second excited states is presumably small compared with the displacements represented by the limiting formulas. On the other hand, in the dyes, where we have shorter molecules and yet a sufficient polarizability to bring the maximum absorption into the red or even the infrared, we may guess that even the first excitation would have an amplitude which would carry the electronic cloud a considerable way toward the limit of displacement.

The amplitude depends upon the polarizability of the molecule, which is greater for those dyes whose absorption bands come at low frequency. We therefore expect from our model that, in a series of similar dyes, those having x bands of lowest frequency will have the highest values of $\bar{\nu}'/\bar{\nu}$. We shall now see that this is the case.

Second Order Bands in Dyes.—All the dyes that we have investigated show pronounced second order x bands. Of the eight dyes in Table II the curves for fluorescein, rhodamine B and malachite green are shown in the paper just preceding.[4] In these three cases the x' band has been identified as such and differentiated from the neighboring y band by the method of fluorescent polarization. The curves for methylene blue, and methylene blue with one proton attached, have also been previously given.[5] Our curves for capri blue and the ion of Michler's hydrol have not yet been published.

The ultraviolet absorption spectrum of crystal violet showed a peculiarity that we have not succeeded in interpreting, except to show that it is due to the B isomer. There is an additional band at 27,500 cm.$^{-1}$ as shown in Fig. 5, but this band is only 55% as high in chloroform as in alcohol and

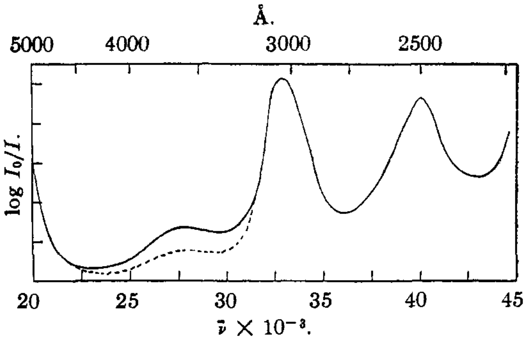


Fig. 5.—The ultraviolet absorption spectrum of crystal violet: upper curve in ethanol; lower curve in chloroform. Both curves are drawn to the same arbitrary extinction at 33 × 10^3 cm.$^{-1}$. The measurements of the chloroform solution extend only to 41 × 10^3 cm.$^{-1}$ where the solvent absorption becomes great. This figure shows that the band at 27500 cm.$^{-1}$ belongs to the B isomer.

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[4] Lewis and Bigeleisen, This Journal, 65, 2102 (1943).

[5] Lewis and Bigeleisen, *ibid.*, 65, 1144 (1943).

it has been shown[6] that the percentage of B isomer drops in this same ratio in going from alcohol to chloroform.

TABLE II

		Solvent	$\bar{\nu}$, cm.$^{-1}$	$\bar{\nu}'$, cm.$^{-1}$	$\bar{\nu}'/\bar{\nu}$	ϵ'/ϵ
1	Fluorescein	Dil. alkali	20400	35100	1.72	0.144
2	Rhodamine B	Dil. alkali	18000	32300	1.80	.137
3	Crystal violet (A)	Ethanol	16940	32900	1.94	.258
4	Michler's hydrol	Gl. acetic acid	16670	33300	2.00	.165
5	Malachite green	Ethanol	16000	31700	1.98	.197
6	Methylene blue	Ethanol	15200	30700	2.02	.109
7	Capri blue	Ethanol	15100	32750	2.17	.153
8	Methylene blue (D^1H^{++})	$3M$ H_2SO_4	13500	29500	2.20	.110

This is a remarkable series in which ϵ'/ϵ is always large and $\bar{\nu}'/\bar{\nu}$ increases almost regularly with increasing wave length of the x band. This is just the trend that was predicted from our potential curve.

In the course of a number of investigations it has been shown how the absorption spectra of dyes are affected by acid, basic and amphoteric addition,[5] by isomerism[6,7] and by polymerization.[8] In three cases[6,9,10] the spectrum of the interesting isomer of the phosphorescent state has been studied. It has been shown how subsidiary vibrational bands may be recognized[8] and how y bands may be distinguished from x bands,[3,4] by studying, with polarized light, molecules that are oriented either by photochemical processes in a rigid solvent, or by excitation to the fluorescent state. In the present paper we have found the second order x bands of dyes and by the use of such data as are given in Tables I and II we can predict the approximate position of these x' bands in similar dyes. We believe that by these various means it is possible to classify all of the bands commonly found for dyes in the infrared, the visible, and the near ultraviolet. Thus it will be possible with greater security to attack the main problem of ascertaining the laws that relate color to chemical constitution.

Summary

Additional second order x bands have been sought and found in the absorption spectra of the cyanines and numerous dyes. In the latter group it has been necessary to make use of an extended potential diagram for electronic oscillations. In this group, the diagram leads to the conclusion that the ratio of the second order frequency to the first order frequency should increase as the first order frequency diminishes. This has been found to be true experimentally.

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[6] Lewis, Magel and Lipkin, THIS JOURNAL, **64**, 1774 (1942).

[7] Lewis, Magel and Lipkin, *ibid.*, **62**, 2973 (1940).

[8] Lewis, Goldschmid, Magel and Bigeleisen, *ibid.*, **65**, 1150 (1943).

[9] Lewis, Lipkin and Magel, *ibid.*, **63**, 3005 (1941).

[10] Lewis and Lipkin, *ibid.*, **64**, 2801 (1942).

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS, ILLINOIS INSTITUTE OF TECHNOLOGY]

Raman Spectra of Solutions of Silver Perchlorate in Toluene and in Water

BY M. J. MURRAY AND FORREST F. CLEVELAND

In a previous investigation[1] the Raman spectrum of a saturated solution of benzene in concentrated aqueous silver perchlorate showed that the vibrations of benzene most affected were those involving the carbon–carbon bonds. This was interpreted as indicating a coördination of the silver ion with the aromatic nucleus, in agreement with the ideas of Winstein and Lucas.[2] The behavior of toluene could not be tested in the same manner because this hydrocarbon has only slight solubility in the aqueous perchlorate. However, toluene, in contrast to benzene, is a remarkably potent solvent for anhydrous silver perchlorate even at room temperature. The saturated solution at 25° contains 50.3% of this salt.[3] It was hoped that the Raman spectrum of this solution would give an opportunity for checking independently the relation of the aromatic nucleus to the silver perchlorate without the disturbing influence of water.

For comparison with the spectrum of the nonaqueous solution, spectra of aqueous solutions of silver perchlorate and of mercuric perchlorate were also obtained.

Experimental

Toluene (purified by repeated extraction with concentrated sulfuric acid and by distillation) was saturated with silver perchlorate which had been prepared according to the method of Hill.[4] Turbidity in the solution was very effectively removed by centrifuging. Four-hour excitation by Hg 4358 Å. yielded a number of Raman lines without producing excessive continuum on the spectrogram.

An almost saturated aqueous solution of mercuric perchlorate was prepared by dissolving mercuric oxide in 70% perchloric acid. After adding a little water and a slight excess of perchloric acid the solution was filtered repeatedly through a sintered glass funnel. Spectrograms obtained for this solution were remarkably free of background.

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[1] Taufen, Murray and Cleveland, THIS JOURNAL, **63**, 3500 (1941).

[2] Winstein and Lucas, *ibid.*, **60**, 836 (1938).

[3] Hill and Miller, *ibid.*, **47**, 2702 (1925).

[4] Hill, *ibid.*, **43**, 254 (1921).