

## CHANGES IN THE FREQUENCY OF THE $B_u$ -TRANSITION IN LINEAR CONJUGATED MOLECULES INDUCED BY DISTURBANCES IN THE TERMINAL CARBON ATOMS

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*The theory of the local state spectrum for the Huckel model of heteropolyenes, recently proposed by the authors, is used to examine the possibility that perturbation of the terminal carbon atoms might affect the frequency of the  $B_u$ -transition in polyenes of arbitrary length. It is shown for the first time that the position of the  $B_u$  band in the spectrum can depend on the extent of the perturbation in a non-monotonic manner. The anomalous behavior of the frequency of the  $B_u$ -transition as a function of the heteropolyene parameters is explained by the presence in the  $\pi$ -electron spectrum of in-gap local levels. The results obtained permit the prediction of absorption band positions for the lowest dipole-allowed 0-0 electron transitions in neutral and ionic forms of heteropolyenes of the types  $X-(CH)_{2N}-X$ ,  $X^+-(CH)_{2N}-X^-$  and  $X-(CH)_{2N}-CH_2$  and hence to suggest synthetic routes for conjugated molecules and polymeric materials which are optically active in the range required.*

It is well known that the absorption frequencies and luminescence of conjugated molecules of the type  $X-(CH)_N-Y$  depend to a considerable extent on the nature of the end groups [1, 2]. This has been used effectively to produce polymethine dyes with absorption bands in required positions. Success has been largely due to the well-developed microscopic theory of the optical properties of this class of molecule. It is no surprise that this theory applies only to compounds with an odd number of methylene groups  $N = 2N_d - 1$ , where  $N_d = 1, 2, \dots$ . When  $N$  is even, i.e., in the case of substituted polyenes, the role of the end groups has been the subject of dispute and controversy (see [3]). In particular, even in the simplest cases which can be considered as the replacement of the terminal carbon atoms by heteroatoms (e.g., oxygen atoms) there has been effectively no study of the effect of such substitution at the microscopic level on the change in absorption frequency and other optical properties.

In this paper we have used the recently proposed theory of the  $\pi$ -electron spectrum of heteropolyenes based on the Huckel model [4] to analyze the relationship of the frequency of the lowest dipole-allowed  $B_u$ -transition to the character parameters, the type of substitution and the type of polyene (neutral or ionic). The results cited below provide the basis for making conjugated molecules which absorb in a desired frequency range. In the broader view, understanding the electronic structure of linear polyenes and the possibilities for modifying it is extremely important for the solution of a whole range of problems, from elucidation of the mechanism of sight to the production of stable polymers with high conductivity.

### MODEL

One of the principal differences between substituted and unsubstituted polyenes and polymethine dyes is the alternation of C-C bonds. As quantum chemical calculations have shown [5] this alternation depends very weakly on the nature of the end groups and the length of the chain, but is strongly linked with the type of molecule: in the neutral form the terminal bonds are double whereas in the ionic doubly charged form the terminal C-C bonds are single. These results are used to check the

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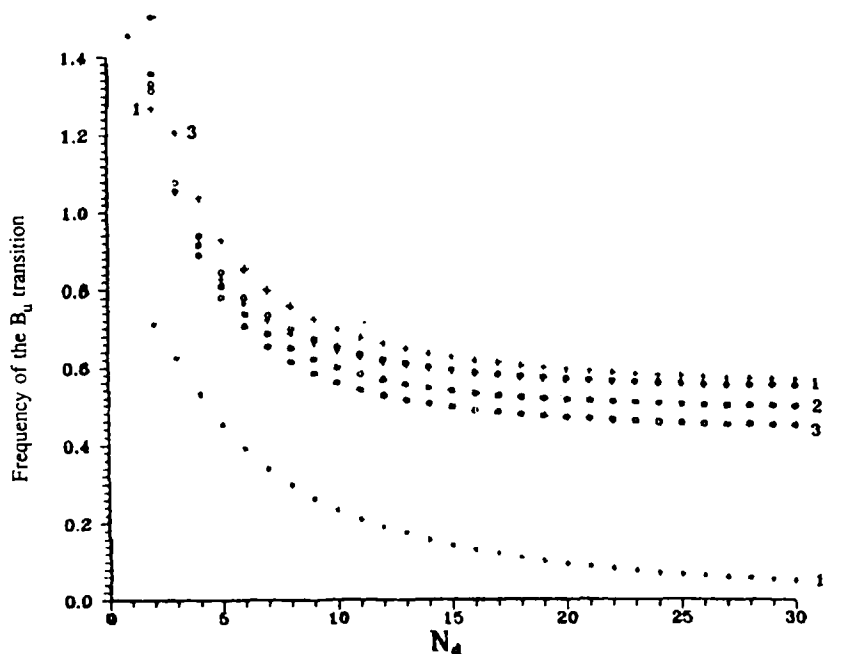


Fig. 1. Dependence of the frequency of the  $B_u$  transition on the length of symmetric heteropolyenes in neutral and ionic forms: o)  $\nu(N_d)$ ; \* )  $\nu^{--}(N_d)$ ; + )  $\nu^{++}(N_d)$ . The numbers by the curves correspond to the values of the perturbation  $\varepsilon = 1, 2$ , or  $3$ . The curves \* for  $\varepsilon = 2$  and  $3$  are practically the same as that shown in the figure.

correctness of the present study. It is suggested that the basic perturbation resulting from the heterosubstituent is the difference between the coulomb integrals of the heteroatoms and the carbon atoms:  $\alpha_{X(Y)} - \alpha_C = \varepsilon_{X(Y)}$ . Neglecting for simplicity the small dependence of the alternation (parameter  $\eta$ ) on the number of bonds and limiting the discussion to substitution of the types  $X-(CH)_{2N_d}-X$  ( $\varepsilon_X = \varepsilon_Y = \varepsilon$ ),  $X^+-(CH)_{2N_d}-X^-$  ( $\varepsilon_X = -\varepsilon_Y = \varepsilon$ ) and  $X-(CH)_{2N_d}-CH_2$  ( $\varepsilon_X = \varepsilon$ ,  $\varepsilon_Y = 0$ ) leads to a three parameter model of the heteropolyenes in which the absolute value of the resonance integral along the C-C bonds of the nonalternating chain is used as the energy scale (for a more complete description of the model see [4]).

The frequency of the  $B_u$ -transition  $\nu$  (in the dianionic and dicationic forms this frequency is given the symbols  $\nu^{--}$  and  $\nu^{++}$  respectively) is determined by the energy gap between the energy of the lowest unoccupied molecular orbital, LUMO, and the energy of the highest occupied molecular orbital, HOMO. In the analysis of the dependence of this frequency on the length of the heteropolyene and the size of the perturbation at the terminal atoms we shall use experimental values of the alternation parameter  $|\eta| = 0.1333$  [6], with  $\eta > 0$  corresponding to terminal double bonds, and  $\eta < 0$  to terminal single bonds, i.e., it agrees with the discussion above on the determination of the frequency of the  $B_u$ -transition, namely that in a neutral polyene the alternation parameter is positive and in the ionic species it is negative. In order to compare the results shown below relative to the frequency of the  $B_u$ -transition with the experimental values it is necessary to use a value of the resonance integral equal to 30305 (cf [6]).

**Frequency of the  $B_u$ -Transition as a Function of the Length of the Heteropolyene.** The influence of the perturbation of the terminal atoms of a polyene on the frequency of the  $B_u$ -transition depends considerably on the length of the molecule (strictly speaking on the ratio between the values of  $N_d$  and  $|\eta|$ ). We shall therefore turn first to symmetrical heteropolyenes and a discussion of the functions  $\nu(N_d)$ ,  $\nu^{++}(N_d)$ , and  $\nu^{--}(N_d)$  calculated for typical values of perturbation of the coulomb integral  $\varepsilon = 1, 2$  and  $3$  (Fig. 1). Note that because of its symmetrical properties,  $\nu(N_d)$  is independent of the sign of  $\varepsilon$ , whereas the dependence of  $\nu^{--}$  on  $N_d$  at  $\varepsilon < 0$  is the same as that of  $\nu^{++}(N_d)$  shown in Fig. 1. The same correspondence occurs for  $\nu^{++}$  at  $\varepsilon < 0$  and  $\nu^{--}$  at  $\varepsilon > 0$ . This remains true for cases of asymmetric substitution, so we can safely limit discussion to positive values of  $\varepsilon$ .

The relationships obtained are clearly groups relative to the limiting value of the transition frequency in an infinitely long molecule. These values are given in Table 1 where  $E_{in}^\infty$  is a known function of the parameters  $\varepsilon$  and  $\eta$  [4]. In the general case the limiting values of the frequency can vary within the limits of the variable  $4 \sinh |\eta|$  and they depend not only on

TABLE 1. Asymptotic Values of the Frequencies of the  $B_u$  Transitions in Heteropolyenes. The Definitions of  $\nu^{++}$  and  $\nu^{--}$  Correspond to  $\varepsilon > 0$ . When  $\varepsilon < 0$ ,  $\nu^{++}$  and  $\nu^{--}$  Change Places. The Value of  $E_{in}^\infty$  is Related to  $\eta$  and  $\varepsilon$  as Follows  $\sqrt{2[\cosh(2\eta) = \cosh(2\eta - \ln f)]}$ , where  $f = (\sqrt{(\varepsilon^2 - 1)^2 + 4\varepsilon^2 \exp(4\eta)} + 1 - \varepsilon^2)/2$ ,  $\varepsilon^2 = \varepsilon^2 \exp(2\eta)$  [4]; for  $|\eta| \ll 1$   $E_{in}^\infty = \sqrt{(4\eta - \ln f) \ln f}$

Type	Frequency of the $B_u$ transition, units of $ \beta $		
	$\lim_{N_d \rightarrow \infty} \nu$ $ \varepsilon  > \exp(-\eta)$	$\lim_{N_d \rightarrow \infty} \nu^{++}$ $ \varepsilon  < \exp( \eta )$	$\lim_{N_d \rightarrow \infty} \nu^{--}$ $ \varepsilon  < \exp( \eta )$
$X-(CH)_{2N_d} - X$	$2 \sinh \eta + E_{in}^\infty$	$2 \sinh  \eta  + E_{in}^\infty$	$2 \sinh  \eta  - E_{in}^\infty$
$X^+-(CH)_{2N_d} - X^-$	$2E_{in}^\infty$	$2 \sinh  \eta  - E_{in}^\infty$	$2 \sinh  \eta  - E_{in}^\infty$
$X-(CH)_{2N_d} - CH_2$	$2 \sinh \eta + E_{in}^\infty$	$2 \sinh  \eta $	$2 \sinh  \eta  - E_{in}^\infty$

Type	Frequency of the $B_u$ transition, units of $ \beta $		
	$\lim_{N_d \rightarrow \infty} \nu$ $ \varepsilon  < \exp(-\eta)$	$\lim_{N_d \rightarrow \infty} \nu^{++}$ $ \varepsilon  > \exp( \eta )$	$\lim_{N_d \rightarrow \infty} \nu^{--}$ $ \varepsilon  > \exp( \eta )$
$X-(CH)_{2N_d} - X$	$4 \sinh \eta$	$4 \sinh  \eta $	0
$X^+-(CH)_{2N_d} - X^-$	$4 \sinh \eta$	0	0
$X-(CH)_{2N_d} - CH_2$	$4 \sinh \eta$	$2 \sinh  \eta $	0
$H_2C-(CH)_{2N_d} - CH_2$	$4 \sinh \eta$	$2 \sinh  \eta $	$2 \sinh  \eta $

the parameters mentioned but also on the type of substitution and form of the heteropolyene. However when  $|\eta| \ll 1$ , which in practice can be considered to be always true, and with the values of  $\varepsilon$  of interest to us,  $E_{in}^\infty$  is either equal to or close to the value of  $2 \sinh |\eta|$ . Then, as seen from Table 1, the limiting frequencies for neutral and dianionic forms of the heteropolyenes of all three types are close to the values of  $4 \sinh |\eta|$  and 0, respectively. The limiting frequencies of the  $B_u$ -transition for the dicationic forms of the heteropolyene depends strongly on the type of substitution. In addition to the two values mentioned above, which are characteristic for  $(X-(CH)_{2N_d}-X)^{++}$  and  $(X^+-(CH)_{2N_d}-X^-)^{++}$ , it has a value of  $2 \sinh |\eta|$  for unsymmetrical substitution (see Table 1). Thus to judge from the limiting values of the transition frequency alone, which can be readily calculated from the formulas in Table 1, the dependence of the absorption frequency on the length of heteropolyenes of different forms and (or) types of substitution should differ only in detail, but this difference is very important quantitatively. It should also be noted that if the limiting values of the frequencies are different from zero, they can be divided into two fields of  $N_d$  values in which the decrease in the absorption frequency with increasing length of the heteropolyene occurs rapidly when  $\eta N_d \ll 1$  and slowly when  $\eta N_d \gg 1$  (see Fig. 1).

One characteristic of these relationships deserves special note – the increase in the effect of the substituents at the terminal atoms on the absorption frequency  $\nu$  in the neutral heteropolyenes with the increase in  $N_d$ . This effect, which is paradoxical at first glance, is explained by the appearance in the longer heteropolyenes of in-scale local states and their peculiar distribution within the scale of the long molecules [4]. A similar effect cannot occur, of course, in polymethine dyes in which there is not alternation of the C–C bonds. Another important difference between the effects of heterosubstituents in polyenes discussed here and the case of polymethine dyes is that in the latter replacement of the terminal atoms by heteroatoms always leads to an increase in the frequency of the  $B_u$ -transition [7] except for extremely short molecules, while perturbation of the

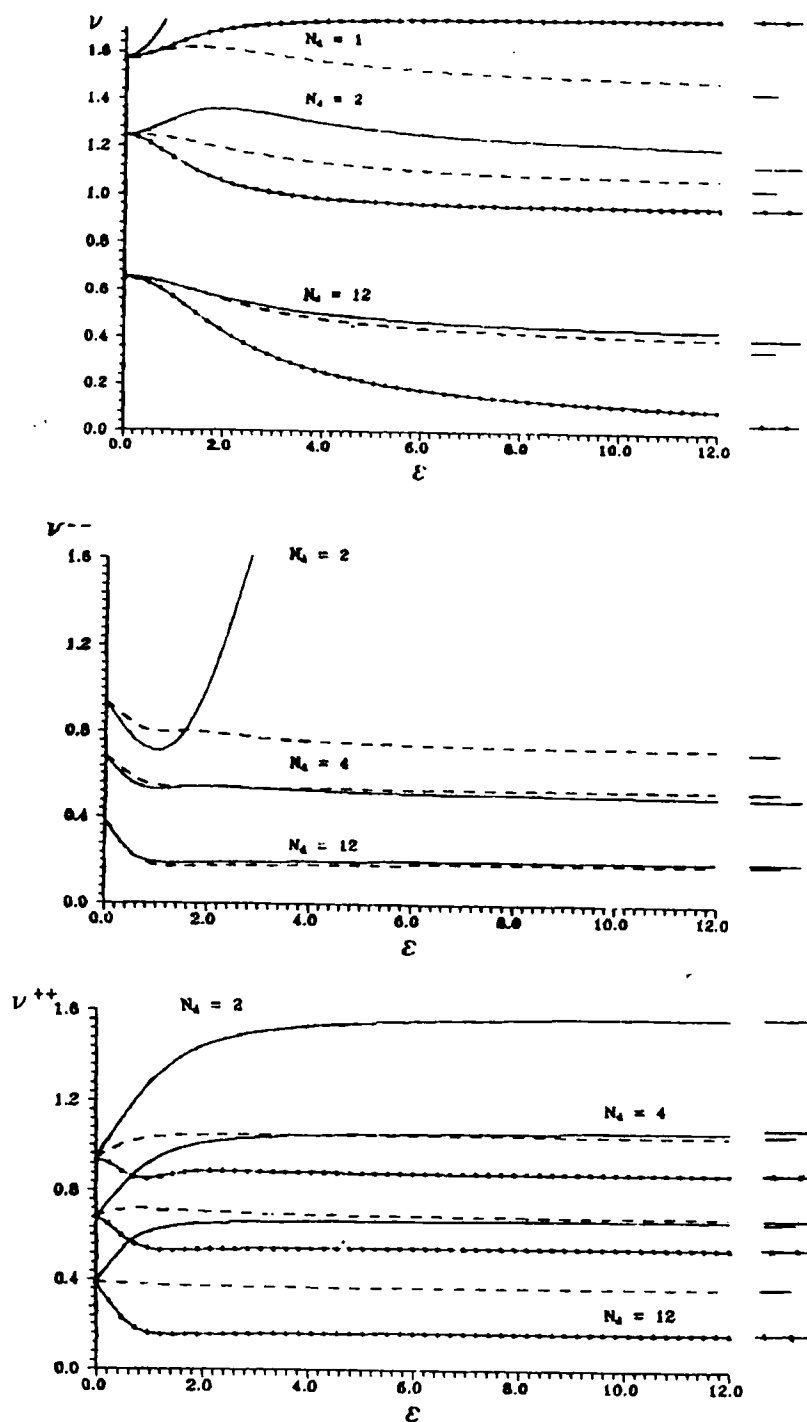


Fig. 2. Dependence of the frequencies of the  $B_u$ -transition on the perturbation parameter  $\varepsilon$  in neutral and ionic forms of the heteropolyenes of the types  $X-(CH)_{2N_d}-X$  (continuous lines),  $X^+-(CH)_{2N_d}-CH_2$  (broken lines) and  $X^+-(CH)_{2N_d}-X^-$  (crossed continuous lines). The values of the frequencies  $\nu$ ,  $\nu^{--}$  and  $\nu^{++}$  in the limit  $|\varepsilon| \rightarrow \infty$  are shown as elongated extensions for  $X-(CH)_{2N_d}-X$ , short extensions for  $X^+-(CH)_{2N_d}-CH_2$  and as extensions with spots for  $X^+-(CH)_{2N_d}-X^-$ .

polyene chain can result in either an increase or a decrease in this frequency. Which of these two effects is to be expected depends on a number of factors which are discussed in the next section.

**Frequency of the  $B_u$ -Transition as a Function of Perturbation of the Coulomb Integral  $\epsilon$ .** In the case of an infinitely strong perturbation of the terminal atoms, the absorption frequency of the neutral forms of heteropolyenes may be defined as:

$$\nu(\epsilon, N) \Big|_{|\epsilon| \rightarrow \infty} = \begin{cases} \nu^{++}(\epsilon = 0, N - 2) = \nu^{--}(\epsilon = 0, N - 2), & X - (\text{CH})_{2N_d} - X \\ \nu(\epsilon = 0, -\eta, N - 2), & X^+ - (\text{CH})_{2N_d} - X^- \\ \nu^+(\epsilon = 0, N - 1) = \nu^-(\epsilon = 0, N - 1), & X - (\text{CH})_{2N_d} - \text{CH}_2 \end{cases} \quad (1)$$

where  $N = 2N_d + 2$ . In other words, in the limit  $|\epsilon| \rightarrow \infty$  the frequency of the  $B_u$ -transition for  $X - (\text{CH})_{2N_d} - X$  has the same value as in the ionic form of the unsubstituted polyene with two less atoms than the initial heteropolyene, and for  $X^+ - (\text{CH})_{2N_d} - X^-$  its value is the same as that for the hypothetical unsubstituted polyene (with opposite alternation) also two atoms shorter, while for  $X - (\text{CH})_{2N_d} - \text{CH}_2$  the transition frequency coincides with the singly charged hypothetical polymethine molecule with one less atom in the chain. The values of the frequency of the  $B_u$ -transitions for the ionic forms of the heteropolyenes within the same limits are determined similarly.

It is convenient to discuss separately the dependence of the frequency of the  $B_u$ -transition on the size of the perturbation of the Coulomb integral of the terminal atoms for the different types of substitution.

In the case of a symmetrical heteropolyene (continuous curves in Fig. 2) the function  $\nu(\epsilon)$  is not monotonic for the shortest molecules but decreases monotonically when the length of the heteropolyene is sufficiently long. The behavior of  $\nu(\epsilon)$  with  $N_d = 1$  has a clear explanation: participation of an extra-regional local state. The qualitative change in the character of the dependence of  $\nu(\epsilon)$  on the increase in chain length of the heteropolyene is connected with the appearance of in-scale local states. Thus the continuous curves in Fig. 2 have maxima ( $N_d = 2$ ) corresponding to fulfillment of the condition  $2|\eta| > \ln((N_d + 2)/(N_d + 1))$  when in-scale local states are not formed for any value of  $\epsilon$  [4]. When the reverse inequality is fulfilled, i.e., when in-scale local states are formed at definite values of the perturbation, the dependence of  $\nu(\epsilon)$  shows a monotonic decrease (curve  $N_d = 12$ ). If  $2|\eta| \approx \ln((N_d + 2)/(N_d + 1))$ ,  $\nu$  is practically independent of  $\epsilon$ .

It is interesting to note that with infinitely strong perturbation of the terminal atoms [the values of  $\nu$  in this case (see (1)), are shown in Fig. 2 as separate sections to the right of the curves] the effect may be either positive (an increase in the frequency of the transition) or negative, depending on the value of the alternation parameter and the ratio of  $\eta$  to  $N_d$ . It is clear from Eq. (1) that if the equation  $\nu(\epsilon = 0, N) = \nu^{--}(\epsilon = 0, N - 2)$  has a solution relative to  $N_d$ , say  $x = N_d$  at a given value of  $\eta$ , then with  $N_d < x$  the effect will be positive and if  $N_d > x$  the effect will be negative. For example  $x = 5$  at  $\eta = 0.035$ . With a realistic value of  $\eta = 0.1333$  the effect of infinitely large perturbation of the terminal atoms appears as a decrease in  $\nu$  for any length of the symmetrical heteropolyene except for the special case where  $N_d = 1$ .

The dependence is qualitatively different for the ionic forms of the symmetric heteropolyene from that discussed above. With  $N_d = 1$ ,  $\nu^{--}$  tends to zero with increasing  $\epsilon$ , since with large perturbation of the HOMO, the LUMO is described as an extra-scale local state. The minimum at  $N_d = 2$  is connected with the extra-scale local state. At larger values of  $N_d$  the frequency  $\nu^{--}$  decreases noticeably with increase in  $\epsilon$  only to a value of approximately 1 and is practically independent of the perturbation of the terminal atoms with  $\epsilon > 1$ . The function  $\nu^{++}(\epsilon)$ , the frequency of the  $B_u$ -transition in the dicationic form of the symmetric heteropolyene, increases monotonically with  $\epsilon$  for any length of the molecule. In contrast to the neutral forms, the effect of perturbation of the terminal atoms for the dicationic form is greater in the shorter molecules.

The dependence of the frequency of the  $B_u$ -transition on  $\epsilon$  reflects the fact that the effect of perturbation on the different  $\pi$ -electron levels of the polyene is not uniform. The nonmonotonicity of this relationship indicates the change in the character of this influence: if, for example, the frequency initially increases with increasing  $\epsilon$  and then falls, it means that initially the energy of the LUMO increases more rapidly than the increase in energy of the HOMO and then the situation reverses. This anomalous behavior of the energy levels on perturbation is explained by the character of the in-scale local states. In heterosubstituted polymethines, where local states cannot arise because of bonds of alternating length, the behavior of the frequency of the  $B_u$ -transition as a function of  $\epsilon$  is "normal", i.e., in cationic and anionic forms of symmetrical heterosubstituted polymethines it increases ( $\epsilon > 0$ ) or decreases ( $\epsilon < 0$ ) monotonically as a function of  $|\epsilon|$ . This behavior corresponds to the intuitive expectation that "positive" perturbation would affect the levels in the upper part of the spectrum more strongly and that "negative" perturbation would affect more strongly the levels in the lower part of the spectrum. The behavior of the heteropolyenes is a long way from these intuitive expectations and it is impossible to predict the effect of such perturbations

on the frequency of the  $B_u$ -transitions without a detailed analysis of the dependence of the energies of the in-scale local levels on the perturbation.

We shall now discuss briefly the dependence of the frequency of the  $B_u$ -transition on  $\varepsilon$  for neutral and ionic forms of the heteropolyenes of types  $X^+-(CH)_{2N_d}-X^-$  (continuous curves with crosses in Fig. 2) and  $X^+-(CH)_{2N_d}-CH_2$  (broken curves).

In neutral and dianionic forms of the asymmetric heteropolyenes  $\nu(\varepsilon)$  and  $\nu^{--}(\varepsilon)$  behave as monotonically decreasing functions of  $\varepsilon$  for any length of molecule except for  $N_d = 1$  or 2 (the exclusion of  $N_d$  is explained by participation of an extra-scale local state in the electronic transition). The behavior of the frequency of the  $B_u$ -transition as a function of  $\varepsilon$  in the dicationic form of the asymmetric heteropolyene is qualitatively analogous to that for the symmetrical heteropolyene, but the dependence on the perturbation is much weaker. Apart from a few values of the chain length, the effect of single and double substitution of the terminal atoms on the change in the frequency of the  $B_u$ -transition is similar. In contrast, the effect of single and double substitution may even be qualitatively different at small values of  $N_d$  (compare the continuous and broken curves for  $\nu(\varepsilon)$  with  $N_d = 2$ ).

In systems of the type  $X^+-(CH)_{2N_d}-X^-$  the function  $\nu(\varepsilon)$  is nonexistent at  $N_d = 1$  and does not increase at larger values of  $N_d$  (continuous curves with spots, Fig. 2). In ionic forms of this type of heteropolyene the relationship  $\nu^{--}(\varepsilon) = \nu^{++}(\varepsilon)$  is always a nonmonotonic function with a minimum, because in the given case the local in-scale states cause a sharply decreased frequency of the  $B_u$ -transition with a change in  $\varepsilon$  from zero to  $\sim 1$ . With larger values of  $\varepsilon$ ,  $\nu^{--}$  is practically independent of the size of the perturbation.

## CONCLUSIONS

The results presented above on the dependence of the absorption frequency on length and on the size of the perturbation of the terminal atoms of polyenes encompass all three possible stable forms of the basic types of heteropolyenes. The dependence is shown to be considerably more complex than in the case of the very similar heterosubstituted polymethines and the effects are determined by a whole complex of factors: the type of substitution, the form of the heteropolyene, the ratio between values of the alternation parameter and the length of the molecule and finally, the extent of the perturbation.

Comparison with experiment showed that considerable shifts in the absorption band are to be expected for typical differences in the Coulomb integrals for the heteroatoms and carbon atoms and for very moderate chain lengths. In particular, one of the results obtained here is the predicted considerable and opposite shifts of the absorption frequency of hexatriene with single (decrease in  $\nu$ ) or double (increase in  $\nu$ ) replacement of the terminal carbon atoms by oxygen atoms. Since in polymeric materials of the polyacetylene type conjugation of the carbon atoms is destroyed by different types of defect, including foreign atoms, the effects described here of substitution at the ends of polyenes might be used to modify the optical properties of conjugated polymers. Finally, the use of the Huckel model to understand the principles of the electronic structure of linear conjugated molecules should be emphasized. In this connection, the results obtained in this paper permit very broad possibilities for all types of experimental verification.

## REFERENCES

1. A. V. Kachkovskii, The Structure and Color of Polymethine Dyes [in Russian], Nauk. Dumka, Kiev (1989).
2. N. Tyutyulkov, J. Fabian, A. Mehlhorn, et al., Polymethine Dyes. Structure and Properties, St. Kliment Ohridski University Press, Sofia (1991).
3. C. Rulliere, A. Declémy, Ph. Kottis, and L. Ducasse, Molecules in Physics, Chemistry and Biology, Kluwer Acad. Publ., Vol. 2, 349-364 (1988).
4. L. I. Malysheva and A. I. Onipko, Teor. Éksp. Khim. (1995).
5. A. D. Kachkovskii and M. L. Dekhtyar', Teor. Éksp. Khim., **28**, No. 4, 313-319 (1992).
6. B. E. Kohler, J. Chem. Phys., **93**, No. 8, 5838-5842 (1990).
7. G. G. Dyadyusha, V. M. Rozenbaum, and M. L. Dekhtyar', Teor. Éksp. Fiz., **100**, No. 3(9), 1051-1060 (1991).