Densities of vibrational states in isotopically substituted polyacetylene by the renormalization-group technique

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A matrix formulation of the renormalization-decimation method is given to evaluate analytically the average density of vibrational states for randomly disordered polymeric chains. The method is preliminarily applied to the distribution of isotopic defects in *trans*-polyacetylene. Good qualitative agreement with the available experimental data is obtained.

INTRODUCTION

The purpose of the present paper is to extend the formalism of the renormalization-group (RG) method[1–4] already applied to the calculation of the density of the vibrational states for linear alloys to the lattice dynamics of a polymeric chain containing isotopic defects. Of particular interest is the application of this method to the case of polyacetylene, for which extensive experimental studies on the effect of deuteration on the in-plane vibrations are available[5] and for which a reliable force field has been recently proposed.[6] It is shown that, despite the approximations involved in the RG method, the calculated spectra are consistent with the experimental observations.

THEORETICAL MODEL

Lattice dynamics of a regular periodic one-dimensional array consisting of an infinite number of translational units may be described by the eigenvalue equation[7,8]

$$(\underline{M}\omega^2-\underline{\Phi})\underline{U}=\underline{0} \tag{1}$$

and by the associated inhomogeneous equation[5,6]

$$(\underline{M}\omega^2-\underline{\Phi})\underline{G}(\omega^2)=\underline{1} \ . \tag{2}$$

In Eqs. (1) and (2), $\underline{M}$ is an infinite diagonal matrix whose diagonal submatrices $\underline{m}$ of dimensions $N\times n$ contain the masses of the atoms in the unit cell, and ω^2 are the eigenvalues of the dynamical matrix $\underline{M}^{-1/2}\underline{\Phi}\underline{M}^{-1/2}$. $\underline{U}$ represents the eigenvector matrix and $\underline{G}(\omega^2)$ is the Green's-function matrix.[7,8]

Here $\underline{\Phi}$ is the infinite interaction matrix in Cartesian coordinates defined as

$$\underline{\Phi}=\underline{\tilde{B}}\underline{F}_R\underline{B} \ , \tag{3}$$

where $\underline{B}$ is the transformation matrix between internal and Cartesian coordinates,[9] and $\underline{F}_R$ is the matrix of the force constants defined in the internal coordinates basis.[9] For an infinite chain, matrices $\underline{B}$, $\underline{F}_R$, and $\underline{\Phi}$ exhibit a periodic block-structured form. For the sake of simplicity we will report here only the structure of the $\underline{\Phi}$ matrix,

$$\underline{\Phi}=\begin{bmatrix} \cdots & & & & & \cdots \\ & \underline{\Phi}_0 & \underline{\Phi}_1 & \underline{\Phi}_2 & \underline{\Phi}_3 & \\ & \underline{\Phi}_{-1} & \underline{\Phi}_0 & \underline{\Phi}_1 & \underline{\Phi}_2 & \\ & \underline{\Phi}_{-2} & \underline{\Phi}_{-1} & \underline{\Phi}_0 & \underline{\Phi}_1 & \\ & \underline{\Phi}_{-3} & \underline{\Phi}_{-2} & \underline{\Phi}_{-1} & \underline{\Phi}_0 & \\ \cdots & & & & & \cdots \end{bmatrix} . \tag{4}$$

The dimension of each square matrix $\underline{\Phi}_i$ is given by $N\times n$, where N is the number of atoms contained in each unit cell and n is the degree of freedom of each atom. In Eq. (4) $\underline{\Phi}_0$ represents the interactions between the atoms belonging to the unit cell, and $\underline{\Phi}_i$ represents the interactions between the atoms of the nth unit cell and those of the $(n+i)$th unit cell. In Appendix A the elements of $\underline{\Phi}_0,\underline{\Phi}_1,\underline{\Phi}_{-1},\underline{\Phi}_2,\underline{\Phi}_{-2}$ obtained by developing Eq. (3) are reported. It is shown that $\underline{\Phi}_{-i}=\underline{\tilde{\Phi}}_i$.

For the evaluation of the spectral properties of a system it is useful to define the normalized Green's-function matrix[7]

$$\underline{g}=\underline{M}\underline{G} \ , \tag{5}$$

which allows a direct calculation of the density of the squared vibrational frequencies[8]

$$\rho(\omega^2)=\mp\frac{1}{\pi}\,\mathrm{Im}\,\mathrm{Tr}\underline{g}(\omega^2\pm i\epsilon), \quad \epsilon\to 0^+ \ . \tag{6}$$

The density of the vibrational states is given by[10]

$$\rho(\omega)=2\omega\rho(\omega^2) \ . \tag{7}$$

Let us develop Eq. (2) by neglecting all the interaction matrices beyond the nearest-neighbors interaction matrix $\underline{\Phi}_1$. We consider a reference unit cell labeled 0 and we label $1,2,\ldots$ $(\bar{1},\bar{2},\ldots)$ the cells to the right (left) of the reference one. The result is

$$\begin{aligned} &\cdots \\ (\underline{m}\omega^2-\underline{\Phi}_0)\underline{G}_{0\bar{2}} &= \underline{\Phi}_1\underline{G}_{0\bar{3}}+\underline{\tilde{\Phi}}_1\underline{G}_{0\bar{1}} , \\ (\underline{m}\omega^2-\underline{\Phi}_0)\underline{G}_{0\bar{1}} &= \underline{\Phi}_1\underline{G}_{0\bar{2}}+\underline{\tilde{\Phi}}_1\underline{G}_{00} , \\ (\underline{m}\omega^2-\underline{\Phi}_0)\underline{G}_{00} &= \underline{1}+\underline{\Phi}_1\underline{G}_{0\bar{1}}+\underline{\tilde{\Phi}}_1\underline{G}_{01} , \\ (\underline{m}\omega^2-\underline{\Phi}_0)\underline{G}_{01} &= \underline{\Phi}_1\underline{G}_{00}+\underline{\tilde{\Phi}}_1\underline{G}_{02} , \\ (\underline{m}\omega^2-\underline{\Phi}_0)\underline{G}_{02} &= \underline{\Phi}_1\underline{G}_{01}+\underline{\tilde{\Phi}}_1\underline{G}_{03} , \\ &\cdots \end{aligned} \tag{8}$$

The dots indicate the remaining equations of this infinite set.

This system can be solved to get $\underline{G}_{00}$ by using the decimation-renormalization procedure proposed by Gonçalves da Silva and Koiller[1] for the calculation of the local density of states in a linear chain. One obtains

$$\underline{G}_{00}=(\underline{m}\omega^2-\underline{\Phi}_0-\underline{P}_\infty-\underline{Q}_\infty)^{-1} , \tag{9}$$

where

$$\begin{aligned} \underline{P}_\infty &= \lim_{n\to\infty} \underline{P}_n , \\ \underline{Q}_\infty &= \lim_{n\to\infty} \underline{Q}_n , \end{aligned} \tag{10}$$

and

$$\begin{aligned} \underline{P}_n &= \underline{P}_{n-1}+\underline{\tilde{R}}_{n-1}(\underline{m}\omega^2-\underline{\Phi}_0-\underline{P}_{n-1}-\underline{Q}_{n-1})^{-1}\underline{R}_{n-1} , \\ \underline{Q}_n &= \underline{Q}_{n-1} \\ &\quad +\underline{R}_{n-1}(\underline{m}\omega^2-\underline{\Phi}_0-\underline{P}_{n-1}-\underline{Q}_{n-1})^{-1}\underline{\tilde{R}}_{n-1} , \\ \underline{R}_n &= \underline{R}_{n-1}(\underline{m}\omega^2-\underline{\Phi}_0-\underline{P}_{n-1}-\underline{Q}_{n-1})^{-1}\underline{R}_{n-1} , \end{aligned} \tag{11}$$

$$\begin{aligned} \underline{P}_0 &= \underline{Q}_0=0 , \\ \underline{R}_0 &= \underline{\Phi}_1 . \end{aligned} \tag{12}$$

The recursion relations (11) are solved numerically for each value of ω^2+i0^+. When convergence is reached, $\underline{g}_{00}$ provides the density of the vibrational states according to Eqs. (5)–(7).

The procedure just discussed, which consists essentially in the elimination, at each step, of the odd-numbered unit cells followed by a renormalization of the parameters which define the dynamics of the system, cannot be directly applied when second-neighbor interaction matrices need to be considered. This is the case of polyacetylene, where long-range force constants arising from delocalized π electrons are to be taken into account. To overcome this difficulty, we have increased the dimension of the translational cells in such a way that the second-neighbor interactions appear in the $\underline{\Phi}_1$ matrix. A more general but much more complicated way to tackle this problem has been proposed in the literature.[11,12]

The density of the vibrational states in an ordered one-dimensional array of translational cells, here evaluated by the use of the decimation-renormalization technique, can also be calculated by alternative conventional methods.[13–15] However, for randomly disordered chains conventional methods allow only numerical simulation of the density of vibrational states for chains with a finite number of atoms. The renormalization technique has been successfully applied to evaluate the local density of the phonon states for the isotopically disordered linear chain.[1] In the following we will discuss the phonon spectrum of an infinite zigzag chain with isotopic disorder only.

We take the cell at the origin to be of type A and consider an isotopically disordered chain $(\ldots AABA \ldots)$. According to Gonçalves da Silva and Koiller and with reference to Eq. (8), in the first step (which consists in the elimination of the odd terms), we substitute into the even $\underline{G}$ matrices (which are considered A-type cells) the odd $\underline{G}_{0j}$ matrices properly averaged:

$$\begin{aligned} \underline{G}_{0,j} &= x_A(\underline{m}_A\omega^2-\underline{\Phi}_0)^{-1}(\underline{\Phi}_1\underline{G}_{0,j-1}+\underline{\tilde{\Phi}}_1\underline{G}_{0,j+1}) \\ &\quad +x_B(\underline{m}_B\omega^2-\underline{\Phi}_0)^{-1}(\underline{\Phi}_1\underline{G}_{0,j-1}+\underline{\tilde{\Phi}}_1\underline{G}_{0,j+1}) . \end{aligned} \tag{13}$$

In Eq. (13), x_A (x_B) are the probability weights $(x_A+x_B=1)$ and $\underline{m}_A$ $(\underline{m}_B)$ are the matrices of the masses for an A (B) -type cell.

The decimation-renormalization procedure is then repeated by keeping fixed the cell at the origin and by relabeling the cells. Thus, in the second stage, the even $\underline{G}$ matrices become odd numbered and are averaged according to

$$\begin{aligned} \underline{G}_{0,j} &= x_A(\underline{m}_A\omega^2-\underline{\Phi}_0-\underline{P}_1-\underline{Q}_1)^{-1}(\underline{R}_1\underline{G}_{0,j-1}+\underline{\tilde{R}}_1\underline{G}_{0,j+1}) \\ &\quad +x_B(\underline{m}_B\omega^2-\underline{\Phi}_0-\underline{P}_1-\underline{Q}_1)^{-1}(\underline{R}_i\underline{G}_{0,j-1}+\underline{\tilde{R}}_1\underline{G}_{0,j+1}), \quad i,j \text{ odd} \end{aligned} \tag{14}$$

where

$$\begin{aligned} \underline{P}_1 &= x_A\underline{\tilde{\Phi}}_1(\underline{m}_A\omega^2-\underline{\Phi}_0)^{-1}\underline{\Phi}_1 \\ &\quad +x_B\underline{\tilde{\Phi}}_1(\underline{m}_B\omega^2-\underline{\Phi}_0)^{-1}\underline{\Phi}_1 , \\ \underline{Q}_1 &= x_A\underline{\Phi}_1(\underline{m}_A\omega^2-\underline{\Phi}_0)^{-1}\underline{\tilde{\Phi}}_1 \\ &\quad +x_B\underline{\Phi}_1(\underline{m}_B\omega^2-\underline{\Phi}_0)^{-1}\underline{\tilde{\Phi}}_1 , \\ \underline{R}_1 &= x_A\underline{\Phi}_1(\underline{m}_A\omega^2-\underline{\Phi}_0)^{-1}\underline{\Phi}_1 \\ &\quad +x_B\underline{\Phi}_1(\underline{m}_B\omega^2-\underline{\Phi}_0)^{-1}\underline{\Phi}_1 . \end{aligned} \tag{15}$$

After $(n-1)$ renormalizations one obtains

$$\begin{aligned} \underline{P}_n &= \underline{P}_{n-1}+x_A\underline{\tilde{R}}_{n-1}\underline{S}_{A,n-1}\underline{R}_{n-1} \\ &\quad +x_B\underline{\tilde{R}}_{n-1}\underline{S}_{B,n-1}\underline{R}_{n-1} , \\ \underline{Q}_n &= \underline{Q}_{n-1}+x_A\underline{R}_{n-1}\underline{S}_{A,n-1}\underline{\tilde{R}}_{n-1} \\ &\quad +x_B\underline{R}_{n-1}\underline{S}_{B,n-1}\underline{\tilde{R}}_{n-1} , \\ \underline{R}_n &= x_A\underline{R}_{n-1}\underline{S}_{A,n-1}\underline{R}_{n-1}+x_B\underline{R}_{n-1}\underline{S}_{B,n-1}\underline{R}_{n-1} , \end{aligned} \tag{16}$$

$$\underline{S}_{A,n-1}=(\underline{m}_A\omega^2-\underline{\Phi}_0-\underline{P}_{n-1}-\underline{Q}_{n-1})^{-1} ,$$
$$\underline{S}_{B,n-1}=(\underline{m}_B\omega^2-\underline{\Phi}_0-\underline{P}_{n-1}-\underline{Q}_{n-1})^{-1} , \quad (17)$$

$$\underline{P}_0=\underline{Q}_0=\underline{0} ,$$
$$\underline{R}_0=\underline{\Phi}_1 . \quad (18)$$

Finally,

$$\underline{G}_{00}^{A}=(\underline{m}_A\omega^2-\underline{\Phi}_0-\underline{P}_{\infty}-\underline{Q}_{\infty})^{-1} , \quad (19)$$

where the index A indicates the type of cell taken as the origin and where

$$\underline{P}_{\infty}=\lim_{n\to\infty}\underline{P}_n ,$$
$$\underline{Q}_{\infty}=\lim_{n\to\infty}\underline{Q}_n . \quad (20)$$

An equation similar to Eq. (19) holds for a B-type cell chosen as the origin. The local densities of states are defined by[1]

$$\rho^{\alpha}(\omega)=-\frac{2\omega}{\pi}\,\mathrm{Im}\mathrm{Tr}[\underline{m}_{\alpha}\underline{G}_{00}^{\alpha}(\omega^2+i\epsilon)] ,$$
$$\epsilon\to 0^+, \quad \alpha=A,B . \quad (21)$$

The average local density of states is given by[1]

$$\rho(\omega)=x_A\rho^A(\omega)+x_B\rho^B(\omega) . \quad (22)$$

As an application of this method a simple example is explicitly worked out in Appendix B.

RESULTS AND DISCUSSION

The theory presented in the previous section has been applied to the calculation of the density of the vibrational states in *trans*-$(CH)_x$, *trans*-$(CD)_x$, and in the copoly(acetylene + acetylene-d_2).

The long-range interactions which arise in polyacetylene from the electron-phonon coupling generate non-negligible $\underline{\Phi}_2$ and $\underline{\Phi}_3$ matrices. In such a case, formulas (16) and (17) of the present paper cannot be applied. It is, however, possible to overcome this difficulty by considering a repeating unit containing two monomeric units. This enables us to extend the interactions in the dynamical matrix up to the second neighbors ($\underline{\Phi}_{\pm 2}$). The matrix $\underline{\Phi}$ then takes the following structure:

$$\begin{bmatrix} \cdots & & & & & \cdots \\ & \begin{bmatrix}\underline{\Phi}_{-2} & \underline{\Phi}_{-1}\\ \underline{0} & \underline{\Phi}_{-2}\end{bmatrix} & \begin{bmatrix}\underline{\Phi}_{0} & \underline{\Phi}_{1}\\ \underline{\Phi}_{-1} & \underline{\Phi}_{0}\end{bmatrix} & \begin{bmatrix}\underline{\Phi}_{2} & \underline{0}\\ \underline{\Phi}_{1} & \underline{\Phi}_{2}\end{bmatrix} & & \\ & & \begin{bmatrix}\underline{\Phi}_{-2} & \underline{\Phi}_{-1}\\ \underline{0} & \underline{\Phi}_{-2}\end{bmatrix} & \begin{bmatrix}\underline{\Phi}_{0} & \underline{\Phi}_{1}\\ \underline{\Phi}_{-1} & \underline{\Phi}_{0}\end{bmatrix} & \begin{bmatrix}\underline{\Phi}_{2} & \underline{0}\\ \underline{\Phi}_{1} & \underline{\Phi}_{2}\end{bmatrix} & \\ & & & \begin{bmatrix}\underline{\Phi}_{-2} & \underline{\Phi}_{-1}\\ \underline{0} & \underline{\Phi}_{-2}\end{bmatrix} & \begin{bmatrix}\underline{\Phi}_{0} & \underline{\Phi}_{1}\\ \underline{\Phi}_{-1} & \underline{\Phi}_{0}\end{bmatrix} & \begin{bmatrix}\underline{\Phi}_{2} & \underline{0}\\ \underline{\Phi}_{1} & \underline{\Phi}_{2}\end{bmatrix} \\ \cdots & & & & & \cdots \end{bmatrix}$$

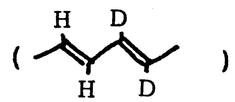
$$=\begin{bmatrix} \cdots & & & & & \cdots \\ & \underline{\Phi}'_{-1} & \underline{\Phi}'_{0} & \underline{\Phi}'_{1} & & \\ & & \underline{\Phi}'_{-1} & \underline{\Phi}'_{0} & \underline{\Phi}'_{1} & \\ & & & \underline{\Phi}'_{-1} & \underline{\Phi}'_{0} & \underline{\Phi}'_{1} \\ \cdots & & & & & \cdots \end{bmatrix} . \quad (23)$$

The somewhat approximate formulation developed in this paper [Eqs. (13)–(22)] can now be applied to the dynamical matrix in Eq. (23). However, it has to be stressed that in this way only random distributions of (C_4H_4), (C_4D_4), $(C_2H_2C_2D_2)$, and $(C_2D_2C_2H_2)$ units are obtained. The density of the vibrational states for a random distribution of the monomers (C_2H_2) and (C_2D_2) cannot be, at present, evaluated.

Figures 1 and 2 show the calculated average densities of vibrational states for different concentrations of (C_4D_4) and $C_2D_2C_2H_2$ defects, respectively. The 1100-cm^{-1} peak of *trans*-$(CH)_x$ shows a progressive shift towards higher wave numbers, accompanied by a lowering in intensity. As the defect concentration is increased the intensity of the $\sim$1500-cm^{-1} peak decreases, while a corresponding increase of the intensity of the $\sim$1400-cm^{-1} peak takes place. It can also be noticed from Fig. 1 that a feature at 820 cm^{-1} appears upon increasing the defect concentration which can be tentatively attributed to a vibration of long C_nD_n sequences. This observation is confirmed by the lack of such a peak in the spectra of Fig. 2.

Of particular interest is the spectral region 800–1000 cm^{-1}, where no peak appears in polyacetylene and where intense peaks are predicted in poly-(C_4D_4) and poly-($C_2D_2C_2H_2$). An unambiguous assignment of the features appearing in Figs. 1 and 2 with increasing defect concentration can therefore be made. The three-peak structure of Fig. 1 can be attributed to C_4D_4 defects embedded in the $(CH)_x$ lattice, while the two-peak structure of Fig. 2 refers to $C_2D_2C_2H_2$ defects.

A further check on the validity of the present approach can be obtained from Fig. 3, where the average density of states for different concentrations of

$M_1 =$ 

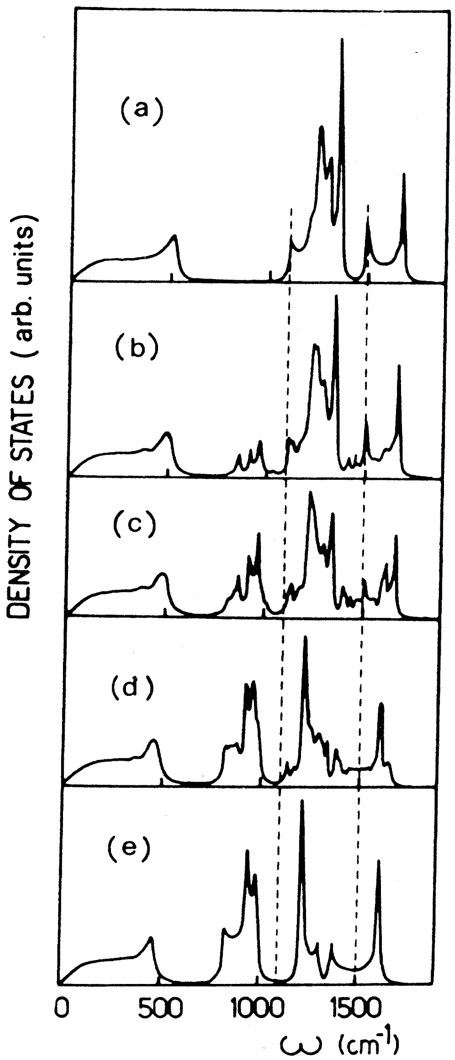


FIG. 1. Evolution of the average density of vibrational states with the concentration of C_4D_4 defects in *trans*-polyacetylene. (a) 0%, (b) 20%, (c) 50%, (d) 80%, and (e) 100% concentration.

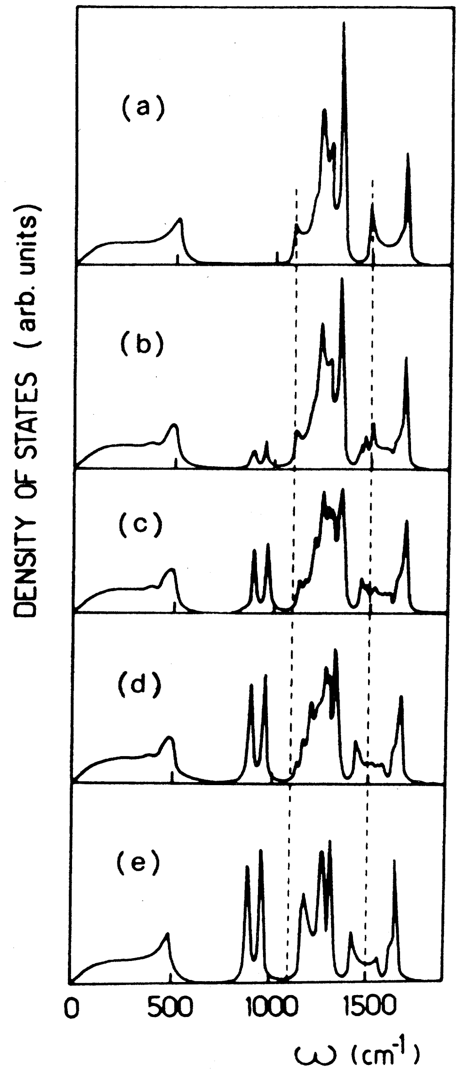


FIG. 2. Evolution of the average density of vibrational states with the concentration of $C_2D_2C_2H_2$ defects in *trans*-polyacetylene. (a)–(e) Same as in Fig. 1.

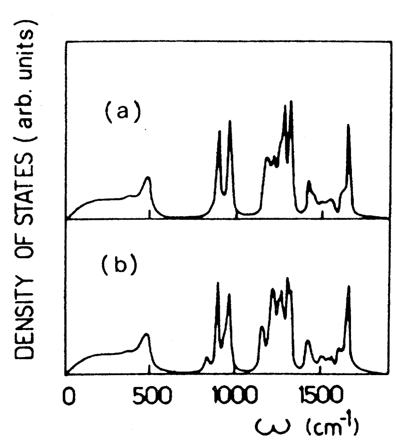


FIG. 3. Average density of vibrational states in *trans*-$(C_2H_2C_2D_2)_x$ for different concentrations of $C_2D_2C_2H_2$. (a) 10%, (b) 50% (see text).

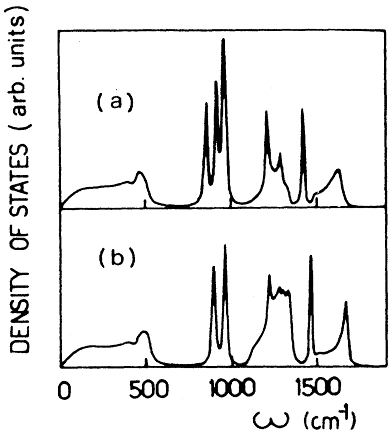
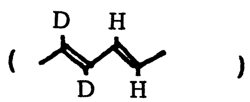


FIG. 4. Local density of vibrational states in *trans*-polyacetylene for the single-impurity limit. (a) C_4D_4 and (b) C_2D_2.

and

$M_2=$ 

are reported. It is seen that by increasing the concentration of M_2 up to 50% the two-peak structure in the region 800–1000 goes into the three-peak structure, which can be attributed to the formation of C_4D_4 islands.

A final confirmation comes from consideration of the local densities of states of isolated C_2D_2 and C_4D_4 defects. It is clear from the formulation discussed above that the calculation is exact in this case. Three defect-induced peaks are detected in the local density of vibrational states at 860, 920, and 965 cm^{-1} for a single C_4D_4 sequence embedded in the $(CH)_x$ lattice [Fig. 4(a)], while only two defect-induced peaks are observed at 890 and 960 cm^{-1} for a single C_2D_2 defect [Fig. 4(b)].

A comparison with the experimental data reported in Ref. 6 shows that the present calculations account, at least qualitatively, for the main experimental features observed in the Raman spectra upon progressive deuteration of the sample. This is true even for high defect concentrations, where one could in principle expect the method to be less accurate. Previous calculations on a random $C_2H_2C_2D_2$ finite copolymer (consisting of 50 CH units) have already been performed using a 39-parameter force field.[16]

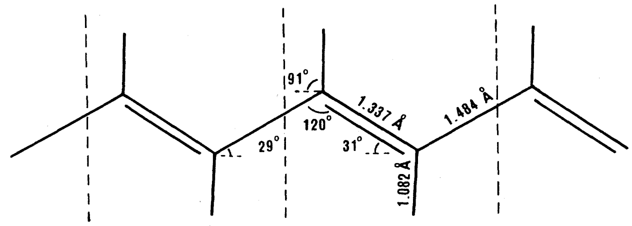


FIG. 5. Geometry of *trans*-polyacetylene (the translational unit cell is indicated with dashed lines).

Further work is in progress to clarify the potential application of the present approach. In particular, it is our intention to investigate the possibility of applying this method to the study of the configurational defects (solitons, polarons, bipolarons) which are presently believed to be responsible for the unusual electrical properties exhibited by semiconducting polymers.

APPENDIX A

A formalism to obtain a general relation between the tensor force field $\underline{\Phi}$ and the valence force field $\underline{F}_R$ has been presented in Ref. 17 and there applied to the case of diamond. Following this formalism the $\underline{\Phi}_i$ matrices discussed in the text can be related to the $\underline{F}_l$ matrices of the potential interactions, coupling the internal coordinates of the origin cell and the internal coordinates of the lth cell, as follows:

$$\underline{\Phi}_i = \sum_{k,l,m} \tilde{\underline{B}}_k (\underline{F}_R)_l \underline{B}_m \ . \qquad \text{(A1)}$$

In Eq. (A1) $\underline{B}_r$ represents the transformation matrix between the internal coordinates of the origin cell and the Cartesian coordinates of the rth cell and the sum runs only over those k,l,m cells for which $i=-k+l+m$. For the polyacetylene case, whose translational unit cell is indicated with dashed lines in Fig. 5, the only nonnegligible submatrices for the in-plane vibrations are $\underline{B}_{-1}$, $\underline{B}_0$, and $\underline{B}_1$. According to Eq. (A1) the $\underline{\Phi}_i$ $(i=-2,-1,0,1,2)$ submatrices defined in the text are given by

$$\underline{\Phi}_{-2}=\tilde{\underline{B}}_0\tilde{\underline{F}}_2\underline{B}_0+\tilde{\underline{B}}_{-1}\tilde{\underline{F}}_3\underline{B}_0+\tilde{\underline{B}}_1\tilde{\underline{F}}_1\underline{B}_0+\tilde{\underline{B}}_1\tilde{\underline{F}}_2\underline{B}_1+\tilde{\underline{B}}_0\tilde{\underline{F}}_3\underline{B}_1+\tilde{\underline{B}}_{-1}\tilde{\underline{F}}_4\underline{B}_1+\tilde{\underline{B}}_1\underline{F}_0\underline{B}_{-1}+\tilde{\underline{B}}_0\tilde{\underline{F}}_1\underline{B}_{-1}+\tilde{\underline{B}}_{-1}\tilde{\underline{F}}_2\underline{B}_{-1} ,$$

$$\underline{\Phi}_{-1}=\tilde{\underline{B}}_0\tilde{\underline{F}}_1\underline{B}_0+\tilde{\underline{B}}_{-1}\tilde{\underline{F}}_2\underline{B}_0+\tilde{\underline{B}}_1\tilde{\underline{F}}_0\underline{B}_0+\tilde{\underline{B}}_1\tilde{\underline{F}}_1\underline{B}_1+\tilde{\underline{B}}_0\tilde{\underline{F}}_2\underline{B}_1+\tilde{\underline{B}}_{-1}\tilde{\underline{F}}_3\underline{B}_1+\tilde{\underline{B}}_1\underline{F}_1\underline{B}_{-1}+\tilde{\underline{B}}_0\underline{F}_0\underline{B}_{-1}+\tilde{\underline{B}}_{-1}\tilde{\underline{F}}_1\underline{B}_{-1} ,$$

$$\underline{\Phi}_0=\tilde{\underline{B}}_0\underline{F}_0\underline{B}_0+\tilde{\underline{B}}_{-1}\tilde{\underline{F}}_1\underline{B}_0+\tilde{\underline{B}}_1\underline{F}_1\underline{B}_0+\tilde{\underline{B}}_1\underline{F}_0\underline{B}_1+\tilde{\underline{B}}_0\tilde{\underline{F}}_1\underline{B}_1+\tilde{\underline{B}}_{-1}\tilde{\underline{F}}_2\underline{B}_1+\tilde{\underline{B}}_1\underline{F}_2\underline{B}_{-1}+\tilde{\underline{B}}_0\underline{F}_1\underline{B}_{-1}+\tilde{\underline{B}}_{-1}\underline{F}_0\underline{B}_{-1} ,$$

$$\underline{\Phi}_1=\tilde{\underline{B}}_0\underline{F}_1\underline{B}_0+\tilde{\underline{B}}_{-1}\underline{F}_0\underline{B}_0+\tilde{\underline{B}}_1\underline{F}_2\underline{B}_0+\tilde{\underline{B}}_1\underline{F}_1\underline{B}_1+\tilde{\underline{B}}_0\underline{F}_0\underline{B}_1+\tilde{\underline{B}}_{-1}\tilde{\underline{F}}_1\underline{B}_1+\tilde{\underline{B}}_1\underline{F}_3\underline{B}_{-1}+\tilde{\underline{B}}_0\underline{F}_2\underline{B}_{-1}+\tilde{\underline{B}}_{-1}\underline{F}_1\underline{B}_{-1} ,$$

$$\underline{\Phi}_2=\tilde{\underline{B}}_0\underline{F}_2\underline{B}_0+\tilde{\underline{B}}_{-1}\underline{F}_1\underline{B}_0+\tilde{\underline{B}}_1\underline{F}_3\underline{B}_0+\tilde{\underline{B}}_1\underline{F}_2\underline{B}_1+\tilde{\underline{B}}_0\underline{F}_1\underline{B}_1+\tilde{\underline{B}}_{-1}\underline{F}_0\underline{B}_1+\tilde{\underline{B}}_1\underline{F}_4\underline{B}_{-1}+\tilde{\underline{B}}_0\underline{F}_3\underline{B}_{-1}+\tilde{\underline{B}}_{-1}\underline{F}_2\underline{B}_{-1} . \qquad \text{(A2)}$$

In these relations the symmetry requirement $\underline{F}_{-i}=\underline{\tilde{F}}_i$ has been used.

The following considerations can be drawn from Eqs. (A2).

(1) $\underline{\tilde{\Phi}}_0=\underline{\Phi}_0$; $\underline{\Phi}_{-i}=\underline{\tilde{\Phi}}_i$.

(2) In order to apply the present approach to the calculation of the local densities of states in polyacetylene, matrices $\underline{\Phi}_3$ and $\underline{\Phi}_{-3}$ must be neglected. It is clear from inspection of Eqs. (A2) that this approximation implies that all the elements of the $\underline{F}_m$ matrices must be set equal to zero for $m>2$. Moreover, the elements of the $\underline{\tilde{B}}_{-1}\underline{F}_2\underline{B}_0$ and $\underline{\tilde{B}}_0\underline{F}_2\underline{B}_1$ matrices must be zero. This requirement implies that some elements of the $\underline{F}_2$ matrix must also be set to zero. Fortunately, in polyacetylene this latter approximation results to be physically reasonable.

(3) It can be shown that the tensor force field $\underline{\Phi}'$ defined on the coordinates basis of a repeating cell containing two monomeric units is related to the $\underline{\Phi}_i$ matrices according to the following relations:

$$\underline{\Phi}'_0=\begin{bmatrix}\underline{\Phi}_0 & \underline{\Phi}_1\\ \underline{\tilde{\Phi}}_1 & \underline{\Phi}_0\end{bmatrix},\quad \underline{\Phi}'_1=\begin{bmatrix}\underline{\Phi}_2 & \underline{0}\\ \underline{\Phi}_1 & \underline{\Phi}_2\end{bmatrix},\quad \underline{\Phi}'_{-1}=\underline{\tilde{\Phi}}'_1\,. \tag{A3}$$

APPENDIX B

Let us take the case of an infinite linear monatomic chain as in Fig. 6. The translational unit cell indicated with dashed lines contains one particle labeled 0 with mass m_A. The transformation matrix between internal and Cartesian displacement coordinates ($\underline{B}$) is

	...	x_{-2}	x_{-1}	x_0	x_1	x_2	...
⋮	...						...
R_{-1}			1	-1			
R_0				1	-1		
R_1					1	-1	
⋮	...						...

(B1)

hence $\underline{B}_{-1}=0$, $\underline{B}_0=1$, and $\underline{B}_1=1$.

If only diagonal interactions are considered $\underline{F}$ is written as

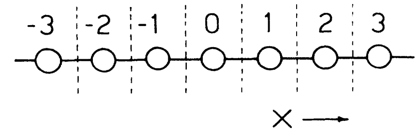


FIG. 6. Linear monatomic chain with mass defects.

$$\underline{F}=\begin{bmatrix}\ddots & & & & & \\ & K & & & & \\ & & K & & & \\ & & & K & & \\ & & & & K & \\ & & & & & \ddots\end{bmatrix}. \tag{B2}$$

By using the equations for $\underline{\Phi}_i$ developed in Appendix A, one gets $\underline{\Phi}_0=2K$ and $\underline{\Phi}_1=-K$. By substituting these values into Eqs. (16) and (17) of the present paper the same analytical expressions developed in Ref. 1 for the case of randomly disordered alloys $A_{x_A}B_{x_B}$ are obtained.

Indeed, by defining

$$\nu=\omega^2,\quad \nu_0^A=\frac{K}{m_A},\quad \nu_0^B=\frac{K}{m_B}\,, \tag{B3}$$

it can be shown that

$$\begin{aligned}
&\underline{R}_n=-m_A\nu_n^A\,,\\
&\underline{P}_n=\underline{Q}_n=\underline{P}_{n-1}+\underline{R}_n=-m_A\sum_{i=1}^{n}\nu_i^A\,,\\
&\nu_n^A=\nu_{n-1}^A\left[\frac{x_A\nu_{n-1}^A}{2\bar{\nu}_{n-1}^A-\nu}+\frac{x_B\nu_{n-1}^B}{2\bar{\nu}_{n-1}^B-\nu}\right],\\
&\bar{\nu}_n^A=\nu_0^A-\sum_{i=1}^{n}\nu_i^A=\bar{\nu}_{n-1}^A-\nu_n^A\,.
\end{aligned} \tag{B4}$$

By inserting these formulas into the normalized $\underline{g}_{00}$ matrix, one gets

$$\underline{g}_{00}^A=m_A\underline{G}_{00}^A=\left[\nu-2\nu_0^A+2\sum_{i=1}^{n}\nu_i^A\right]^{-1}. \tag{B5}$$

An analogous expression can be written for $\underline{g}_{00}^B$.

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