An *ab initio* approach to phonon spectrum of *trans*-polyacetylene

LETTER TO THE EDITOR

An *ab initio* approach to phonon spectrum of *trans*-polyacetylene

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Abstract. By an *ab initio* calculation based on the local density approximation of density-functional theory, the force constants up to the third nearest-neighbour carbon-hydrogen unit are determined to obtain the phonon spectrum of *trans*-polyacetylene for the first time. The calculated phonon frequencies at the Γ point coincide well with those of the observed infrared and Raman spectra of *trans*-polyacetylene. The motion of hydrogen atoms is shown to be important in determining the phonon spectrum of polyacetylene due to the contribution of the bending between the CH and CC bonds.

Trans-polyacetylene [1], as a prototype of conducting polymers, has been studied extensively due to its promising electric, magnetic and optical properties [2]. In particular, Su, Schrieffer and Heeger (SSH) [3] proposed a soliton model to explain these properties of conducting polymers. The resulting physics turned out to be quite rich and the model has been very successful in interpreting the experimental phenomena. However, in the SSH model some approximations have been made to describe *trans*-$(CH)_x$, the main one being that only a translation of the CH group as a whole in the chain direction is considered among the six degrees of freedom for the group. To study the physical properties quantitatively, especially the vibrational spectra in detail, one has to consider all these coordinates.

Vibrational spectra of *trans*-$(CH)_x$ have been studied in many ways. Within the discrete one-dimensional SSH model, all vibrational modes around the soliton excitation [4] as well as in the dimerized lattice [5] are obtained. Three infrared localized modes are found to fit the observed three infrared absorption peaks in doped polyacetylene in total. Furthermore, by use of a two-dimensional model, including the contribution of the bending between the CC bonds, a few more localized modes are found [6], depending on the adjustable model parameters, which are not completely clear for *trans*-$(CH)_x$. Based on *ab initio* second-order Møller–Plesset perturbation calculations of *trans*-oligoenes, Hirata *et al* [7] extrapolated the vibrational force field of *trans*-$(CH)_x$ using scale factors. Although their result seems close to the experimental data, it is still believed that further parameter-free calculations are needed for the phonon spectra.

Ab initio methods based on density-functional theory (DFT) are now common and there are well established tools for studying structual and vibrational properties of materials. The plane-wave pseuodopotential method and local-density approximation (LDA) to DFT have provided a simple framework and the accuracy and predictive power of this method have been demonstrated convincingly in a large variety of systems. The calculation of reliable phonon spectra in semiconductors is well within reach of DFT. In this letter, we report the result of an *ab initio* calculation on the dimerized lattice of *trans*-polyacetylene based on the

local density approximation of density-functional theory without any adjustable parameters. We compute the force constants up to the third nearest-neighbour carbon–hydrogen unit to obtain the in-plane vibrational spectra of a *trans*-polyacetylene chain. The calculated phonon frequencies at the Γ point coincide well with that of the observed infrared and Raman spectra of *trans*-$(CH)_x$. We also show that not only bending between the CC bonds but also the motion of hydrogen atoms is important in determining the phonon spectra of *trans*-$(CH)_x$ due to the contribution of the bending between the CH and CC bonds.

The present numerical calculations were performed using the local-density functional theory [8, 9] and the norm-conserving pseudopotential method [10, 11] on a Hitachi S-3800/380 supercomputer. The Kohn–Sham equations were solved iteratively in terms of a plane-wave basis. The electron density is the only information transmitted from one step to another of the iteration. The total energy of the system was minimized directly by using the conjugate-gradient technique [12]. We employed the non-local norm-conserving pseudopotential [13] for carbon, especially constructed to optimize the softness of the pseudopotential, and thus minimize the size of the basis set needed to represent it. In the case of hydrogen we used the true $1/r$ potential. The calculations were performed on a single *trans*-$(CH)_x$ chain in a supercell with periodic boundary condition. The distance between chains in neighbouring supercells was larger than 7 Å [14], so that the interaction between chains could be neglected. The method of special k points [15] was used to perform the integrations in k space over the first Brillouin zone. Before we continued with the calculation of these forces constants, we carried out a similar calculation to that in [14] to optimize the plane structure of a polyacetylene chain; the constraint of the C_{2h} symmetry was taken into account during the optimization process for the structure. The plane-wave cut-off energy adopted in the calculation was 50 Ry, which gives very good convergence for the total-energy and geometry of the ground state. In figure 1 the optimized structure of *trans*-$(CH)_x$ is shown, which gives a dimerized configuration.
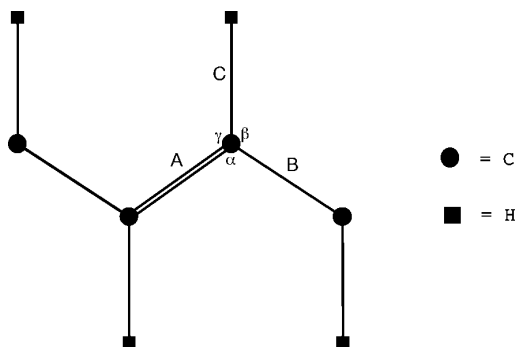
Figure 1. The optimized structure of *trans*-polyacetylene. The lattice constant $a = 2.443$ Å, the double bond $A = 1.345$ Å, the single bond $B = 1.415$ Å, the CH bond $C = 1.103$ Å, the CCC bond angle $\alpha = 124.53°$, and the CCH bond angles $\beta = 117.03°$ and $\gamma = 118.44°$.

The vibrational spectra are determined by a direct diagonalization of the dynamic matrix. This matrix is constructed by finite differencing of the forces at different points close to the equilibrium geometry. The calculation was for a supercell with six carbon–hydrogen units, which allowed us to obtain the force constants up to the third nearest-neighbour CH unit. The cut-off energy was taken to be 40 Ry, since the smaller value of the cut-off energy does not lead to any significant changes in the force constants. In particular, to avoid a possible small deviation in the obtained ground-state geometry away from the exact one,
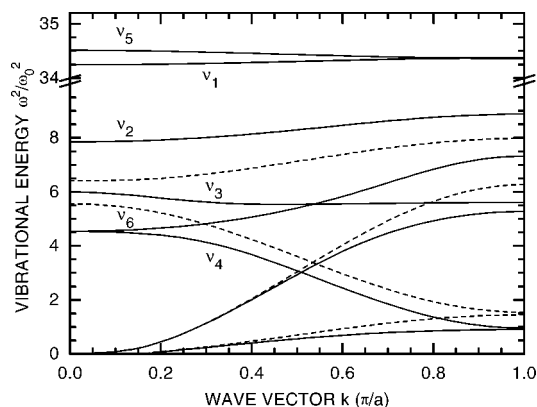
Figure 2. The vibrational energies of *trans*-polyacetylene. The unit of vibrational energies ω_0 corresponds to a frequency of 519.7 cm^{-1}, the wave vector k (in unit of π/a) is for the chain axis. The results with frozen CH bonds (dashed lines) are compared with those considered for all coordinates of the carbon and hydrogen atoms in polyacetylene (solid lines).

we performed the calculations for the Hellmann–Feynman forces for the geometries with two different displacements by small distances (10^{-3} times the size of the supercell)† in the positive and negative directions of the current axis for each non-equivalent atom and coordinate of the primitive unit cell.

The in-plane vibrational dispersion curves of *trans*-polyacetylene are shown in figure 2. Among these eight branches, the lowest two curves are branches of the longitudinal and the transverse acoustic vibrational modes and the $k = 0$ (Γ point) modes are the translational motions parallel and perpendicular to the chain axis; the upper two are the vibrational curves due to the CH bond stretching. The almost dispersionless nature indicates the independent vibrations between the different CH bonds. The high frequencies of the modes also show that the CH bond stretching has no effects on the motion of the carbon backbone. The other four branches correspond mainly to the long-bond stretching mode, the alternating carbon vibration along the chain axis, the CH bond bending with carbon motion perpendicular to the chain axis and the short-bond stretching mode. All these vibrations are connected to the motion of hydrogen atoms perpendicular to the CH bonds. This fact indicates the importance of hydrogen in determining the vibrational structure. However, it is not only the one-dimensional models, such as the SSH Hamiltonian [3], but also these two-dimensional models [6, 16] that neglect the contribution of hydrogen. To see the contribution of hydrogen atoms clearly, we also show the result with frozen CH bonds, i.e. the motion of hydrogen atoms is always set to be the same as that of the associated carbon atoms (shown in figure 2 by dashed lines). The large difference implies that a quantitative (sometime qualitative) description of vibrational structure for polymers should include the contribution of hydrogen atoms. Furthermore, according to the vibrational patterns, vibrational frequencies at the Γ point can be compared with the corresponding observed values [17–19] of the infrared and Raman bands of *trans*-polyacetylene as well as the calculated ones with the scaled force field obtained at the MP2/6-31G* level [7]. We give the comparison in table 1, from which it can be seen that the phonon frequencies we obtained without any adjustable parameters coincide quite well with the observed ones.

† We also calculated the H–F forces with the derivative of a smaller displacement (10^{-4} times the size of the supercell), the results within effective digits are completely the same.

Table 1. The vibrational frequencies (in unit of cm^{-1}) of polyacetylene at the Γ point.

Mode	Symmetry	Present Result[a]	Observed values[b]	MP2/6-31G*[c]
ν_1	a_g	3041	2990	2985
ν_2	a_g	1456	1457	1455
ν_3	a_g	1272	1294	1293
ν_4	a_g	1106	1066	1089
ν_5	b_u	3052	3013	2993
ν_6	b_u	1107	1170	1174

[a] *Ab initio* calculation without any input parameters.
[b] References [17–19].
[c] Calculated value with the scaled force fields obtained at the MP2/6-31G* level [7].

In summary, by an *ab initio* calculation based on the local density approximation of density-functional theory, we have computed the force constants up to third nearest-neighbour carbon–hydrogen unit to obtain the phonon spectrum of *trans*-polyacetylene without any adjustable parameters. The phonon frequencies at the Γ point we obtained coincide well with that of the observed infrared and Raman spectra of *trans*-polyacetylene. We also show that the motion of hydrogen atoms is important in determining the phonon dispertion structure of polymers.

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