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Vibrational frequency and LO–TO splitting determination for planar–zigzag β-poly(vinylidene fluoride) using density-functional theory

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Abstract

We have determined the vibrational frequencies for planar–zigzag β-poly(vinylidene fluoride) using first principles density-functional theory. Specifically, through the use of the generalized gradient approximation, periodic boundary conditions and the computation of longitudinal optical–transverse optical splittings (LO–TO splittings), we have found very good agreement between our vibrational frequencies and those found experimentally and by semi-empirical methods. We also find better agreement than a previous Hartree–Fock density functional determination. We have demonstrated the utility of our method for the accurate determination of vibrational frequencies for other novel ferroelectric co-polymers when experimental force constants may not be available.

Keywords: Ferroelectric polymers; Density-functional theory; Vibrational frequencies

1. Introduction

The ferroelectric behavior of poly(vinylidene fluoride) or PVDF was first reported by Furukawa et al. [1]. Ease of synthesis, low cost, and mechanical flexibility make PVDF and its co-polymers more advantageous for use in some solid-state devices. It is an ideal material for applications in which soft transducers are needed due to its good acoustic impedance.

PVDF or (–CH_2–CF_2–)$_n$ exists in at least five phases, with the β and δ phases exhibiting ferroelectricity. Specifically, β-PVDF (form I) contains *trans* conformations for all carbons in its chains and possesses two formula units per unit cell. It is the presence of the highly electronegative fluorine atoms and their corresponding dipole moment that largely provide this material with its ferroelectric behavior. The spontaneous polarization in this material lies perpendicular to the polymer chain. Lando et al. determined an orthorhombic structure containing a planar–zigzag chain (Fig. 1(a) and (b)) [2]. The planar–zigzag designation refers to all carbon atoms lying within the *yz* plane. They confirmed their structure by nuclear magnetic resonance. Due to the shorter *c*-axis lattice constant reported by Lando et al. compared to a doubled van der Waals radius for fluorine, an alternatively-deflected structure was proposed in which carbon atoms are alternatively deflected away from the *yz* plane [3,4]. We have recently shown that the planar–zigzag structure is the preferred structure at 0 K based upon differences in total energies between the two structures [5].

Understanding and modeling the underlying atomic origin for the ferroelectricity in β-PVDF has centered on the determination of its vibrational spectrum. One of the first studies focused on the confirmation of the planar–zigzag structure for β-PVDF [6]. Enomoto et al. completed a normal mode analysis for β-PVDF using modified Urey–Bradley force constants transferred from polyethylene and tetrafluoroethylene [7]. They were able to assign peaks within their infrared spectrum based upon this analysis. Beorio and Koenig also utilized force constants from polyethylene and tetrafluoroethylene to assign the peaks in their Raman spectrum to specific normal modes [8].

A subsequent determination by Tadokoro et al. [9] used modified valence force field intramolecular force constants from Boerio and Koenig [8,10] (see below). Intermolecular force constants were also determined and included in the computations. The calculated vibrational frequencies were

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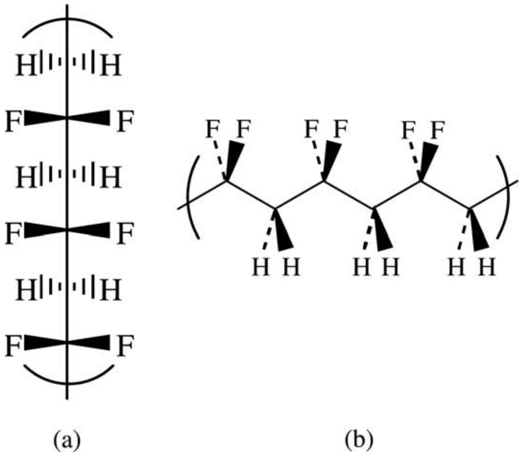

Fig. 1. Planar–zigzag structure for β-poly(vinylidene fluoride) (a) chain-axis view, (b) side view.

compared to experiment and found to have excellent agreement.

When charged atoms vibrate within a crystal lattice, a transition dipole moment is generated for those vibrational modes that are infrared-active. The phonon that originates from this transition dipole moment is a polar phonon. The transition dipoles in turn cause a macroscopic electric field that couples back to the longitudinal optical (LO) modes of the polar phonon. This results in a shifting of the LO modes towards higher frequencies compared to the frequency of the unshifted transverse optical mode (TO). This LO–TO splitting can be observed in spectra of noncentrosymmetric polar crystals, like β-PVDF. It has also been reported in other organic ferroelectric materials [11,12]. Tadokoro et al. subsequently studied the Raman spectrum of poled samples of β-PVDF in order to assess its dipole–dipole interactions via LO–TO splittings [13].

These previous studies utilized experimental results in order to determine force constants from which vibrational frequencies were calculated. Recently, a first-principles determination of the vibrational spectrum of β-PVDF has been completed. Using a restricted Hartree–Fock self-consistent field method, a structurally optimized 11 monomer β-PVDF chain was studied and its vibrational spectrum reported (see below) [14].

Since previous vibrational frequency determinations for β-PVDF have utilized either semi-empirical methods based on experimental results or density-functional methods that do not consider several important characteristics of the system, a more thorough and complete first-principles treatment is warranted. LO–TO splittings can also be included due to existence of polar phonons. We have previously determined the structure of the planar–zigzag structure using the experimental lattice constants and have found excellent agreement with experiment for its bond lengths and angles [5]. Building on that study, a fully relaxed structure (both in atomic coordinates and lattice constants) can be determined and from this structure, the vibrational frequencies for β-PVDF can be found. By also calculating the Born effective charges and dielectric permittivities, it is possible to include the LO–TO splittings into the vibrational frequency determination.

2. Theoretical methodology

Using the ABINIT software package [15,16], we have applied density-functional theory (DFT) with the Perdew–Burke–Ernzerhof implementation of the generalized-gradient approximation (GGA) [17] and periodic boundary conditions. This form of the exchange-correlation functional is parameter-free and has recently been used for the study of PVDF and its co-polymers [18,19]. Optimized pseudopotentials [20] were generated using the OPIUM code [21] for use with a plane-wave basis set cut-off energy of 50 Ry [22]. This energy cut-off allowed for less than 1 mRy basis-set error per angular momentum. We have previously used these same pseudopotentials to study planar–zigzag β-PVDF at the experimentally determined lattice constants [5].

Each unit cell contains two monomer units, one at the origin and the other centered at (1/2, 1/2, 0). The unit cell is orthorhombic with $Cm2m$ (C_{2v}^{14}) space group symmetry. Brillouin zone integrations were done using a 4×4×4 Monkhorst-Pack k-point mesh [23]. Convergence testing showed that the error due to k-point sampling at this mesh was less that 0.001 eV in the total energy per unit cell. Atomic relaxations were completed using Broyden–Fletcher–Goldfarb–Shanno minimization that takes into account the total energy of the system as well as the computed Hellmann–Feynman forces [24,25]. Converged or relaxed atomic positions were achieved when the forces on all atoms were less than 0.02 eV/Å.

In order to determine the vibrational frequencies for β-PVDF, it is important to allow relaxation of all internal coordinates along with the structural parameters. It has been previous shown that a structure found by constrained relaxation (i.e., atomic relaxation at fixed or experimental lattice constants) yields slightly different vibrational frequencies than a structure found by free relaxation (i.e., atomic and structural relaxation) for $PbTiO_3$, a perovskite ferroelectric material [26]. The freely relaxed structure, however, gives a theoretical energy minimum with respect to strain and is more appropriate for the computation of elastic properties and strain–phonon couplings. Initially, we chose the experimentally determined lattice constants according to Hasegawa et al. [3] along with the atomic positions found in our previous work [5]. By computing the stresses for different unit cell dimensions, it is possible to relax the lattice constants to achieve a fully relaxed crystal structure. The full relaxation was terminated when the total stress on the unit cell was less than 1 MPa.

Density-functional perturbation theory has been applied for the determination of the vibrational frequencies [27–31]. First, the dynamical matrix at Γ ($\mathbf{q}=0$) is determined from systematic atomic displacements. Diagonalization of this dynamical matrix will yield the TO mode frequencies ($\overleftrightarrow{D}^{\mathrm{TO}}$). Then by applying a homogeneous electric field and determining the derivative of the wave functions with respect to the electric field, the Born effective charge and dielectric permittivity tensors are found. The Born effective charges provide the amount of charge transfer in a material due to atomic displacement. The *mn*-th TO mode dynamical matrix element can be corrected for the LO–TO splittings according to

$$D_{mn}^{\mathrm{LO}}(\mathbf{j}) = D_{mn}^{\mathrm{TO}}(\mathbf{j}) + \frac{4\pi e^2}{\Omega}\,\frac{Z_m^*(\mathbf{j})Z_n^*(\mathbf{j})}{\varepsilon_\infty(\mathbf{j})},$$

where Ω is the unit cell volume, $Z_m^*(\mathbf{j})$, $Z_m^*(\mathbf{j})$ are the Born effective charges for atoms *m* and *n*, respectively, in the **j**-th direction and $\varepsilon_\infty(\mathbf{j})$ is the dielectric permittivity constant in the **j**-th direction [30,32]. The LO corrected dynamical matrix ($\vec{D}^{\mathrm{LO}}$) can then be diagonalized (taking into account atomic masses) to determine the reported vibrational frequencies.

3. Results and discussion

3.1. Fully relaxed structure for planar–zigzag β-PVDF

As stated above, in order to determine accurate vibrational frequencies, a fully relaxed structure, both in atomic positions and lattice parameters, must be found. Table 1 summarizes the bond lengths and angles in our fully relaxed structure along with its lattice constants. We have also included the bond lengths and bond angles for our previously determined theoretical structure with experimentally determined lattice constants [5] and the experimental results according to Hasegawa et al. [3]. In our fully relaxed structure, we find lattice constants a few percent larger than the experimentally determined values. This amount of overestimation is common with DFT-GGA calculations [33]. However, the bond lengths and angles are almost identical to those of our previous theoretical results, which were in excellent agreement with the experimental results. It is interesting to note that in our present study the C–C–C bond angle is closer to the experimental value. This results from the slight increase of the *c* lattice constant from 2.56 to 2.60 Å.

Table 1
Theoretical and experimental lattice constants, bond lengths and bond angles for planar–zigzag β-poly(vinylidene fluoride)

	Present theory	Previous theory[a]	Experiment[b]
Lattice constants			
a	8.88	8.58	8.58
b	5.09	4.91	4.91
c	2.60	2.56	2.56
Bond lengths			
C–H	1.10	1.10	1.09
C–F	1.39	1.39	1.40
C–C	1.54	1.53	1.54
Bond angles			
H–C–H	107.6	107.5	111.9
F–C–F	105.2	105.3	101.2
C–C–C	112.3	113.6	112.6

Lattice constants and bond lengths are given in Angstroms and bond angles in degrees.

[a] From Ref. [5].

[b] From Ref. [3].

3.2. Vibrational frequencies for planar–zigzag β-PVDF

Based upon the group symmetry C_{2v}^{14}, there should be 14 normal modes plus three translational modes and one lattice librational mode around the chain axis [6,9,13]. Those 14 normal modes can be divided into five modes with A_1 symmetry [$\nu_s(CH_2)$, $\nu_s(CF_2)$, $\nu_s(CC)$, $\delta(CH_2)$, $\delta(CF_2)$], two modes with A_2 symmetry [$t(CH_2)$, $t(CF_2)$], three modes with B_1 symmetry [$\nu_a(CC)$, $w(CH_2)$, $w(CF_2)$], and four modes with B_2 symmetry [$\nu_a(CH_2)$, $\nu_a(CF_2)$, $r(CH_2)$, $r(CF_2)$] [34]. The librational mode will have B_2 symmetry. The normal and librational modes are Raman active. All modes but the A_2 symmetric modes will be infrared active. Since our unit cell contains two polymer chains (double the spectroscopic unit cell), we find doubly-degenerated vibrational frequencies.

Table 2 contains the infrared vibrational frequencies for β-PVDF from the present study. We have grouped the frequencies according to their symmetry. These values were determined from the diagonalization of the TO dynamical matrix ($\vec{D}^{\mathrm{TO}}$) and therefore, should be equal to the infrared experimental values. In addition, we have included the infrared experimental values and those from semi-empirical force constant analysis [13]. For the librational lattice mode, we have used the frequency reported in Ref. [9]. For completeness, we have included the Raman vibrational frequencies for the infrared silent modes (A_2) also from Ref. [9]. The semi-empirical values were found from solving the dynamical secular equations described in terms of the mass-adjusted Cartesian displacement coordinates. Thirty experimentally determined intramolecular force constants of valence force field type were used from previous studies [8,10]. In addition, four intermolecular force constants were determined from the addition of second derivative of the potential energy given by a Lennard–Jones potential (to model the van der Waals interaction) and a Coulombic force constant (to model the electrostatic interaction between chains). For the former term, only the H···F atomic pairings were included since their interatomic distances were less than 3 Å. For the latter term, partial charges for the C and F atoms were deduced from the C–F bond length and dipole moment. An assumed dielectric constant was also needed. Table 2 also includes the potential energy distribution analysis for each vibrational frequency in order to identify the combination of specific normal modes that gives rise the absorbance at a given frequency.

Our vibrational frequencies are in very good agreement with both the experimental and semi-empirical values. The errors in the vibrational frequencies are expected for DFT-GGA calculations for non-metallic insulating systems. More specifically, we find generally lower frequencies than experiment and the semi-empirical values. This underestimation of the vibrational frequencies originates from the increased unit cell volume. An exception to the underestimation occurs in the highest frequency modes, specifically $\nu_s(CH_2)$ and $\nu_a(CH_2)$. The origin of this overestimation may lie in the smaller bond angle with in the $-CH_2-$. The largest amount of error occurs in the librational mode ($\sim$16%). It is important to note that our

Table 2
Theoretical and experimental vibrational frequencies for planar–zigzag β-poly(vinylidene fluoride)

Species	Present	Previous[a]		PED (%)[b]
		Observed	Calculated	
A_1	3015	2980	2975	$\nu_s(CH_2)$ (99)
	1424	1428	1434	$\delta(CH_2)$ (81)
	1213	1273	1283	$\nu_s(CF_2)$ (40) $-$ $\nu_s(CC)$ (22) + $\delta(CCC)$ (26)
	810	840	844	$\nu_s(CF_2)$ (59) + $\nu_s(CC)$ (17)
	482	508	508	$\delta(CF_2)$ (98)
A_2	1022	980[c]	980	$t(CH_2)$ (100)
	258	260[c]	265	$t(CF_2)$ (100)
B_1	1325	1398	1408	$w(CH_2)$ (58) $-$ $\nu_a(CC)$ (34)
	1139	1071	1074	$\nu_a(CC)$ (53) + $w(CH_2)$ (25) $-$ $w(CF_2)$ (22)
	430	468	471	$w(CF_2)$ (90)
B_2	3069	3022	3024	$\nu_a(CH_2)$ (99)
	1159	1177	1177	$\nu_a(CF_2)$ (71) $-$ $r(CF_2)$ (18)
	856	880	883	$r(CH_2)$ (62) $-$ $\nu_a(CF_2)$ (18) $-$ $r(CF_2)$ (19)
	419	442	444	$r(CF_2)$ (70) + $r(CH_2)$ (24)
	81	70[d]	72[c]	Librational lattice mode

Frequencies are given in cm^{-1}.

[a] From Ref. [13]. Observed values are infrared spectral data unless noted.

[b] Potential energy distribution from Ref. [13]. See Ref. [34] for notation. The sign (+/−) indicates the phase relation among the symmetry coordinates.

[c] Raman spectra data from Ref. [9]. These modes are not infrared active.

[d] Infrared spectra data from Ref. [9].

determination did not use any empirical parameters of any kind (other than atomic numbers and masses of the atoms).

As previously stated, a Hartree–Fock DFT determination has been completed for the vibrational frequencies for β-PVDF [14]. No tabulated results were reported for the Hartree–Fock study. Since their study was based upon an 11-monomer chain, bands of frequencies were found. Although numerical comparison is not possible, several comments can be made between our results and theirs based upon the location of these bands. First, the locations of the narrow bands assigned to the anti-symmetric and symmetric CH_2 stretches respectively, (bands I and II, using notation from Ref. [14]) are approximately 300 cm^{-1} higher than our values. Band III, which corresponds to CH_2 bending and wagging predominantly, lies 200 cm^{-1} higher than our reported values for these modes. These differences underscore the inherent concerns with Hartree–Fock calculations of converged monomers. Our calculations incorporate not only the correlation energy of the system but employ periodic boundary conditions. These conditions permit the inclusion of intermolecular effects, which will not be present in a converged monomer study. Lastly, it is important to consider the chain-terminating groups that are present in the chain. Although their identity is not reported in the Hartree–Fock study, these groups will have an effect on a finite chain's dipole moment and may contribute to some of the difference between the theoretical and experimental results [35]. This is avoided in the present study due to periodic boundary conditions.

In a recent vibrational study of PVDF thin films with high β-phase content, an absorption peak at 600 cm^{-1} has been found [36]. This peak was assigned to belong to β-PVDF as compared to the other phases present in the films. This peak was not found in our present study of β-PVDF. Furthermore, this peak has been found in previous vibrational studies of β-PVDF samples; 599 cm^{-1} [6], 598 cm^{-1} [7], 600 cm^{-1} [9]. In the latter study, the absorption is assigned to noncrystalline portions of the sample due to its appearance in the infrared spectra of the α, β and γ forms as well as in molten samples. Based upon our findings, this explanation seems reasonable.

Table 3 contains the LO–TO splittings computed in the present study for several vibrational modes for β-PVDF. The LO frequencies were found from diagonalization of the LO dynamical matrix ($\overleftrightarrow{D}^{LO}$). We have also included the splittings found experimentally. The experimental splittings were found

Table 3
Theoretical and experimental longitudinal optical (LO), transverse optical (TO) frequencies (ω) and (LO–TO) splittings ($\omega_{LO} - \omega_{TO} = \Delta\omega$) for planar–zigzag β-poly(vinylidene fluoride)

Species	Theory			Experiment[a]		
	ω_{LO}	ω_{TO}	$\Delta\omega$	ω_{LO}	ω_{TO}	$\Delta\omega$
A_1	1225	1213	12	1282	1276	6
	815	810	5	842	840	2
	484	482	2	509	508	1
B_2	859	856	3	881	880	1

Frequencies are given in cm^{-1}.

[a] From Ref. [13].

from examining Raman spectra for a poled 40-μm β-PVDF thin film sample using different scattering geometries [13]. Several factors must be considered in assessing the experimental data. First, the thin film gave weak Raman intensities and the signal-to-noise ratio was not high. Also, the frequency shifts are difficult to detect due to the peaks' broadness. The size of the splittings is much smaller than those found in inorganic ferroelectric materials, like $PbTiO_3$ [26]. We find good agreement between the theoretical and experimental results for the LO–TO splittings. To our knowledge, this is the first time these splittings have been computed for this material.

As a final note, it is important to qualify the results based upon our choice of exchange–correlation functional. While it is clear that inclusion of a correlation energy term has improved the vibrational frequencies considerably, higher-level functionals may have yielded further improvements. Furthermore, van der Waals-corrected gradient functionals may also better describe van der Waals interactions in this material and its related co-polymers [37]. However, this method introduces empirical parameters into the calculations.

4. Conclusions

The vibrational frequencies for planar–zigzag β-poly(vinylidene fluoride) have been determined from first principles using density-functional theory and periodic boundary conditions. This determination has included electron correlation effects by employing the generalized gradient approximation. We have also examined longitudinal optical–transverse optical (LO–TO) frequency splitting which arises from the existence of polar phonons within this material. In order to incorporate these splittings into the frequency determination, the Born effective charge and dielectric permittivity tensors were also computed. Our vibrational frequencies are in very good agreement with the experimental and semi-empirical theoretical results. In addition, our results are in better agreement with experiment than those of a previous Hartree–Fock density-functional study. The LO–TO splittings are also in good agreement with experimental findings. Using these methods, it will be possible to predict more accurately the vibrational properties for other ferroelectric co-polymers, when experimentally determined intramolecular and intermolecular force constants are not available.

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