Dynamical and optical properties of the ethylene crystal: Self-consistent phonon calculations using an "ab initio" intermolecular potential

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Using an intermolecular potential from ab initio calculations, we have calculated the structure and solved the lattice dynamics problem of the ethylene crystal in the self-consistent phonon formalism. The aperiodic effects, as included by this formalism, systematically improve the optical mode frequencies, in comparison with experiment, but the corrections to the harmonic frequencies are still substantially too small. The crystal structure and its pressure dependence are well represented. From the phonon polarization vectors we have also evaluated the Raman scattering and infrared absorption intensities of the optical modes, applying a scheme which takes into account the mutual polarization of the molecules (the "local field corrections"). The Raman intensities agree quite well with experiment; the infrared intensities are less realistic, probably due to the neglect of intermolecular overlap effects in the intensity calculations. Using an empirical atom-atom potential for hydrocarbons instead of the ab initio potential, the assignment of the optical lattice modes by their calculated frequencies was not fully consistent with the Raman intensity ratios obtained from their polarization vectors.

I. INTRODUCTION

As a first step in any lattice dynamical study which is not purely phenomenological the potential of the solid must be defined. To date, practically all calculations on molecular crystals have used simple empirical intermolecular potentials, mostly of the atom–atom type1–3 (pairwise additive isotropic interactions between the atoms in different molecules), with parameters fitted to the experimental data. The lattice dynamics is usually treated in the harmonic approximation; sometimes,3–5 the calculated phonon frequencies are included in the optimization of the (atom–atom) potential parameters. The danger of such treatments is that possible deficiencies in the model potential and in the dynamical model are blurred: the fit of the parameters to the experimental data may (partly) compensate these deficiencies.

In the present study of the ethylene crystal we have tried to improve on the usual treatments in three ways. In the first place, we have used an intermolecular potential derived from ab initio calculations,6–9 with no empirical fit parameters. The crystal lattice structure calculated with this potential agrees well with experiment. When used in a harmonic lattice dynamics calculation the potential has yielded fairly good phonon frequencies also, although the best empirically fitted potentials match the experimental data still somewhat better. Part of the remaining discrepancies may originate from the harmonic model, however, and the second characteristic of the present study is that we have used the self-consistent phonon method10 in order to correct for the effects of anharmonicity. Thus, the importance of these effects can be assessed and the temperature and pressure dependence of the crystal properties can be calculated and compared with experiment. The third point concerns the assignment of the phonon modes. The optical modes (wave vector q = 0) can be observed by IR and Raman spectroscopy. The (symmetry) character of these modes is not usually measured, however, except for the distinction between g and u modes in centrosymmetric crystals, which modes are Raman and IR active, respectively. So, if only the frequencies of these modes are obtained from lattice dynamics calculations and compared with optical spectra, the agreement may seem reasonable but some of the modes may be interchanged. Moreover, the frequencies, i.e., the eigenvalues of the dynamical problem, may depend less sensitively on the potential than the corresponding eigenvectors. Therefore, we have provided additional information by calculating also the intensities of the optical modes, which depend on the phonon eigenvectors. For this purpose, we have applied a formalism for the Raman and IR intensities in molecular crystals11,12 which explicitly includes the (electrostatic) long range interactions between the molecules.

II. METHODS AND POTENTIAL

A. Intermolecular potential

The ab initio calculations leading to the ethylene–ethylene potential used in the present studies have been reported in a previous paper,6 as well as the fitting procedure which yields the parameters in the analytical representation of the results. This analytical representation has the form of a pairwise additive isotropic atom–atom potential with distance dependent functions of the exp–6–1 type, just as some of the empirical hydrocarbon potentials2,3 (a Buckingham exp–6 potential, supplemented with Coulombic interactions between
TABLE I. Parameters of the atom—atom potentials used for ethylene (C2H4): 
\[ V(r_{ij}) = -A_{ij} r_{ij}^6 + B_{ij} \exp(-C_{ij} r_{ij}^6) + q_i q_j r_{ij}^2. \]

<table>
<thead>
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<th>Parameters</th>
<th>( V ) (kcal ( \text{mol}^{-1} ))</th>
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<th>( B ) (( \text{kcal} \text{ mol}^{-1} ))</th>
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\( ^a \) Atomic coordinates (in molecular frame): C: \( (\pm 0.6685, 0.0, 0.0) \), H: \( (\pm 1.2335, \pm 0.9275, 0.0) \). 
\( ^b \) Atomic charges shifted to positions: C: \( (\pm 0.5549, 0.0, 0.0) \), H: \( (\pm 1.0095, \pm 0.8308, 0.0) \). 

atomic point charges). The “atomic” point charges have been shifted away from the nuclei, however, since this yields a much better representation of the \( ab \text{ initio} \) calculated (long range) electrostatic interaction between the molecules. The coefficients of the \( r^{-6} \) attractive terms have been obtained by fitting \( r^{-6} \) attractions between the carbon and hydrogen atoms (C-C, C-H, and H-H) to the (long range) anisotropic dispersion interactions between the molecules (from \( ab \text{ initio} \) calculated multipole expansion coefficients). The repulsive exponential terms represent the overlap interactions obtained from an \( ab \text{ initio} \) calculation of the (first order) interaction energy between two ethylene molecules which includes these overlap (charge penetration and exchange) effects by retaining the exact intermolecular interaction operator, instead of its multipole expansion, and using wave functions antisymmetrized over the dimer. The resulting repulsive interactions indeed fall off exponentially with the intermolecular distance. The induction (multipole-induced multipole) interactions are very small and, since these would yield the dominant three-body contributions, we can expect the ethylene crystal potential to have small deviations from pairwise (molecule–molecule) additivity (a few percent of the binding energy at the van der Waals minimum).

The \( ab \text{ initio} \) data have been calculated for eight different orientations of the ethylene molecules and several intermolecular distances. For the long range \( r^{-6} \) interactions the atom–atom model works very well (if the atomic charges are shifted); the fit of the overlap (exponential) terms is somewhat less good, but the orientational and distance dependence of the \( ab \text{ initio} \) potential is reasonably well represented. The parameters determining the analytical “\( ab \text{ initio} \)” potential are collected in Table I, together with the parameters in a recent hydrocarbon atom–atom potential fitted to the experimental data. In Ref. 6 we have seen that the most striking difference between the \( ab \text{ initio} \) potential and various empirical hydrocarbon potentials is that the latter substantially underestimate the electrostatic multipole–multipole interactions between the C2H4 molecules.

B. Self-consistent phonon method; implementation for molecular crystals

The self-consistent phonon (SCP) formalism for lattice dynamics calculations has been developed for applications to the light rare gas crystals (helium, in particular) which have anharmonic interaction potentials in combination with relatively high zero-point vibrational energies. The formalism starts from the following dynamical eigenvalue equations, just as the harmonic model:

\[
D(q)\omega(q) = \omega^2(q)\mathbf{M} \omega(q)
\]

where the tensor \( \mathbf{M} \) contains the masses \( M \) of the atoms in each sublattice \( \sigma \):

\[
M^{\text{add}}_{\sigma\sigma} = M^{\text{add}}_{\text{atom}} \delta_{\sigma\sigma} \delta_{\sigma\sigma} \; (\sigma = x, y, z).
\]

The eigenvalues \( \omega(q) \) and eigenvectors \( \mathbf{e}_q \) are the frequencies and polarization vectors of the phonon modes with wave vector \( q \). In the harmonic approximation \( D \) is the Fourier transform of the force constant matrix \( \phi \):

\[
D^{\text{add}}_{\sigma\sigma}(q) = \sum_i \phi_{\sigma\sigma}^{\text{add}}(l) \exp[iq \cdot \mathbf{R}(l)],
\]

where the force constants are the second derivatives of the potential for the equilibrium structure of the crystal; \( \mathbf{R}(l) \) is the direct lattice vector of the unit cell \( l \). In the SCP method the force constants are replaced by effective force constants which are derived by minimizing the first order expression for the free energy \( F \) of the system, i.e., the canonical ensemble average of the “exact” anharmonic potential \( V \) over the harmonic oscillator states:

\[
F = \sum_{l} \left\{ \frac{\beta}{2} \ln[2 \sinh(\frac{\beta}{2} \omega_j(q))] - \frac{1}{2} \omega_j(q) \coth(\frac{\beta}{2} \omega_j(q)) \right\}
+ \frac{1}{2} N \sum_{\mathbf{R}_{\text{add}}(l)} \left( V(\mathbf{R}_{\text{add}}(l) + \mathbf{u}_{\text{add}}(l)) \right).
\]

The vector \( \mathbf{R}_{\text{add}}(l) \) is defined as \( \mathbf{R}_{\text{add}}(l) = \mathbf{R}(l) + \mathbf{R}_{\sigma} - \mathbf{R}_\sigma \), where \( \mathbf{R}_\sigma \) is the vector joining the origin of the unit cell with the \( \sigma \) sublattice. The relative atomic displacements are \( \mathbf{u}_{\text{add}}(l) = \mathbf{u}_{\sigma}(l) - \mathbf{u}_{\sigma}(0) \) and the vectors \( \mathbf{u}_{\sigma}(l) \) denote the displacements of the \( \sigma \) atoms in unit cell \( l \), relative to their equilibrium positions, \( \mathbf{R}(l) + \mathbf{R}_\sigma \). The temperature enters into the formalism via the quantity \( \beta = \hbar/kT \). The minimization of expression (4) with respect to the effective force constants \( \phi \) leads to the following expression for these force constants:

\[
\phi_{\sigma\sigma}^{\text{add}}(l) = \langle \nabla_{\text{add}} \mathbf{u}_{\text{add}}(l) \rangle.
\]

This means that the second derivatives of the potential \( V \) have now to be averaged over the relative atomic displacements \( \mathbf{u}_{\text{add}}(l) \). The averaging of any quantity \( Q \), whether it is the potential in Eq. (4) or its second derivatives in Eq. (5), can be expressed by means of the displacement–displacement correlation function \( \lambda(\mathbf{R}, \mathbf{R}') \):
\( \langle Q[R_{\alpha\beta}(l) + u_{\alpha\beta}(l)] \rangle = (2\pi)^{-3/2} \left| \det(\lambda) \right|^{-1/2} \times \int du \langle Q[R_{\alpha\beta}(l) + u] \rangle \exp(-\frac{1}{2}u^2 \lambda^{-1} u) \). \hspace{1cm} (6)

These functions \( \lambda \) are given by

\[ \lambda_{\alpha\beta}(q, l) = \langle [u_{\alpha}(l) - u(0)]_{\alpha}(u_{\beta}(l) - u(0))_{\beta} \rangle \]

and they can be calculated from the following expression:

\[ \lambda_{\alpha\beta}(q, l) = \frac{1}{cN} \sum_{i,j} [1 - \cos q \cdot \mathbf{R}(l)] \times \omega_j(q) \cot \beta \omega_j(q) e_j(q)^{\alpha} e_j(q)^{\beta} \,, \hspace{1cm} (8) \]

where \( c \) is the light velocity, if \( e_j(q) \) is normalized as \( e_j(q) \cdot M \cdot e_j(q) = 1 \). Since the expression (8) contains the eigenvalues and eigenvectors of the dynamical Eq. (1), Eqs. (1)–(8) have to be solved self-consistently.

The first application of this formalism to molecular crystals was made by Raich et al. for the \( \alpha \) phase of solid \( N_2 \). Actually, these authors treated the motions of the individual \( N \) atoms, which interact via an intermolecular atom–atom potential and an intramolecular harmonic or Morse type potential describing the \( N_2 \) stretch. Wasiutynski has extended the formalism by considering explicitly the librational motions that occur in molecular crystals. In that case, one has translational displacements \( u^t = (x, y, z) \) and rotational displacements \( u^r = (\varphi, \theta, \psi) \) of the (rigid) molecules; together these are grouped in a six-dimensional displacement vector \( u = (u^t, u^r) = \{u_i; \alpha = 1, \ldots, 6 \} \).

Wasiutynski starts from the same dynamical Eqs. (1), but the dimension of the problem is doubled, since the eigenvectors \( e_j(q) \) have librational components \( e_j(q)^{\alpha} \) for \( \alpha = 4, 5, 6 \). The mass tensor (2) must be extended as follows:

\[ M_{\alpha\beta} = 0 \,, \hspace{1cm} \text{for} \alpha = 4, 5, 6 \text{ and } \beta = 1, 2, 3 \]

and

\[ M_{\alpha\beta} = \delta_{\alpha\beta} \, \gamma \text{, for } \alpha = 1, 2, 3 \text{ and } \beta = 4, 5, 6 \,, \hspace{1cm} (9) \]

where \( \gamma \) is the moment of inertia tensor of the molecules in the \( c \) sublattice (in the crystal system of axes). The effective force constant matrix \( \Phi \) and its Fourier transform \( \Phi \) have mixed translational–rotational \((tr)\) and pure rotational \((rr)\) elements, in addition to the pure translational \((tt)\) elements given by Eq. (5). Also, the displacement–displacement correlation functions (7) and (8) have such components \( \lambda^{tr}, \lambda^{rr}, \lambda^{rt}, \lambda^{rt}, \lambda^{r}, \lambda^{rr}, \text{and } \lambda^{rt} \).

For intermolecular potentials which consist of additive atom–atom contributions (or interactions between generalized force centers of the molecules, such as the potential described in Sec. II A), Wasiutynski has worked out the calculation of the effective force constants (5) in terms of the atomic displacement–displacement correlation functions. These can be related to the molecular functions \( \lambda^{rt}, \lambda^{rr}, \lambda^{rt}, \text{and } \lambda^{rt} \) by substituting into Eq. (7) the following relation between atomic displacements \( u(m) \) and the rigid molecule translations \( u^t \) and rotations \( u^r \):

\[ u(m) = u^t + u^r \times R(m) \,, \hspace{1cm} (10) \]

where \( R(m) \) is the position vector of atom \( m \) relative to the molecular center of mass. It must be realized, however, that Eq. (10) and also the harmonic oscillator kinetic energy expression in terms of \( u^r = (\varphi, \theta, \psi) \) are exact only for infinitesimal rotations \( u^r \). So the SCP method, as generalized to molecular crystals by Wasiutynski, may be less effective in correcting the harmonic model for larger amplitude anharmonic librations. Numerical calculations which have been carried out on the ordered \((\alpha\text{ and } \gamma)\) phases of solid \( N_2 \) (using an \textit{ab initio} interaction potential\textsuperscript{18} similar to the present one) confirm this observation. The SCP corrections for the translational mode frequencies lead to almost perfect agreement with experiment; the librational frequencies, especially at temperatures near the \( \alpha-\beta \) phase transition, remain somewhat in error.

Wasiutynski has applied this generalized SCP method to the cubic hexamethylenetetramine crystal with one molecule in the primitive unit cell.\textsuperscript{18} The application of the formalism to the monoclinic ethylene crystal, space group \( P2_1/n \), with two molecules in the primitive cell, is rather straightforward. The integrations over the atomic displacements (6) which have to be made for the potential, in the free energy expression (4), and for its second derivatives, in the effective force constant matrix (5), have been carried out numerically by Gauss–Hermite quadrature,\textsuperscript{21} using \( 3^{rd} \) and \( 5^{th} \) points, respectively. Nondiagonal terms in the displacement–displacement correlation functions \( \lambda \) appear to be very small; when evaluating expression (6), the off-diagonal terms in \( \lambda^{-1} \) have been neglected. The Heilmholz free energy (4), or the Gibbs free energy \( G = F + pv \) for crystals under constant pressure, has been minimized, not only with respect to the effective force constants as implied by the SCP method, but also with respect to the lattice structure: the unit cell parameters and the positions and orientations of the molecules in the primitive cell (if not determined by the crystal symmetry). This structure optimization is repeated in each SCP iteration. As a starting point for the SCP iterations we have used the eigenvalues and eigenvectors from a harmonic calculation.

The summations over \( q \) in Eqs. (4) and (8) replace exact integrations over the first Brillouin zone, and so it is important to choose a set of wave vectors \( q \) which correctly represent these integrals. In principle, we have chosen a uniform mesh in reciprocal space. The set of \( q \) must reflect the complete symmetry of the crystal, however, including the point group operations. Since the tensor \( \lambda \) given by Eq. (8) transforms under symmetry operations in the same way as the force constant tensor \( \Phi \) [Eq. (5)], one can restrict the set of \( q \) to the fundamental wedge (\( \frac{1}{2} \) of the Brillouin zone) and use the appropriate weight factors and transformation properties in the summations (4) and (8). In this we have taken 312 points.

Finally, it must be mentioned that the lattice sums occurring in Eqs. (3) and (4) have been performed over 42 nearest molecules in the ethylene crystal. The crystall structure is known from x-ray diffraction,\textsuperscript{22} but the monoclinic cell parameters \( a, b, c, \text{ and } \beta \) and the Euler...
angles $\xi$, $\eta$, $\zeta$ corresponding with the equilibrium ori-
entations of the molecules have been optimized in the cal-
bulations (by minimizing the free energy as men-
tioned above). This minimization was carried out by the
program package MINUITS.\textsuperscript{22} The calculations have been
made also for deuterated ethylene, for which the crys-
tal structure under pressure is known.\textsuperscript{24}

C. Raman intensities

In a sample of randomly oriented crystallites as one
has for the Raman measurements on ethylene,\textsuperscript{25} the
polarized Stokes intensity for a nondegenerate lattice
mode $j$ with normal coordinate $Q_j$ and frequency $\omega_j$, is
given by\textsuperscript{26}

$$I_j = \frac{n \omega_j^4}{2 \pi^2 \omega_j^3 (1 - \exp(-\beta \omega_j))} \sum_{\alpha, \delta} \left| \frac{\partial \chi_{\alpha, \delta}}{\partial Q_j} \right|^2,$$  \hspace{1cm} (11)

where $\omega_j$ is the frequency of the scattered light $\omega_s = \omega_0 - \omega_j$. The tensor $\chi$ describes the (high frequency) elec-
tric susceptibility of the crystal. In the simplest ("orien-
ted gas") model the molecules in the crystal are as-
sumed to be noninteracting and the crystal susceptibil-
ity $\chi$ is given by the sum of the molecular polarizability
tensors $\alpha_{\alpha', \delta}'$, expressed in the crystal principal axes
system. Actually, the susceptibility $\chi$ which is the re-
ponse function of the crystal to external electric fields is modified by the interactions between the mole-
cules. The principal correction term to the response
function is due to the internal field from the induced
dipoles, which changes the local field and thereby the
induced dipole moments. Including this term, one ob-
tains\textsuperscript{27}

$$\chi = \frac{4 \pi}{v} \sum_{\alpha, \delta'} (1 - \alpha \cdot L)_{\alpha, \delta'}^{(-1)} \alpha'_{\alpha', \delta'},$$  \hspace{1cm} (12)

where $v$ is the unit cell volume, $\alpha$ is the $3n \times 3n$ tensor
containing the molecular polarizability tensors $\alpha_{\alpha', \delta}' = \delta_{\alpha, \alpha'} \alpha_{\delta}'$, $L$ is the $3n \times 3n$ Lorentz tensor which is com-
posed of $3 \times 3$ Lorentz tensors $L_{\alpha, \delta}$,\textsuperscript{27} and $n$ is the num-
ber of sublattices. In principle, other correction terms
due to higher multipoles, to overlap interactions, and
to dispersion forces between the molecules should be
included as well. We expect the induced dipole field
correction term to be dominant, however, as it is for
the collision induced (depolarized) Raman intensities in
compressed gases\textsuperscript{19} and therefore we have neglected
all other interaction terms.

In crystals where the molecules lie on centers of
symmetry (such as ethylene) the optical (q = 0) modes
are Raman active. In that case, the susceptibility
derivative simplifies to\textsuperscript{11}

$$\frac{\partial \chi}{\partial Q_j} = \sum_{\alpha} \sum_{\alpha'} \frac{\partial \chi}{\partial u_{\alpha, \alpha'}} (e_{\alpha'})_{\alpha'},$$  \hspace{1cm} (13)

where $(e_{\alpha'})_{\alpha'}$ are the (rotational) components ($\alpha = 4, 5, 6$)
of the eigenvector for the librational mode $q$ (with $q = 0$)
which multiply the rotational displacements $u' = (\theta_\alpha, \theta_\beta, \theta_\gamma)$ of the molecules. From Eq. (12), noting that the
Lorentz tensors $L$ do not change by rotational displace-
ments (they depend only on the molecular positions), one
finds, after some manipulation,\textsuperscript{11}

$$\frac{\partial \chi}{\partial u_{\alpha, \alpha'}} = \frac{4 \pi}{v} \sum_{\alpha', \delta'} (1 - \alpha \cdot L)_{\alpha, \alpha'}^{(-1)} \frac{\partial \alpha_{\delta'}}{\partial u_{\alpha, \alpha'}} (1 - L \cdot \alpha)_{\delta'}^{(-1)},$$  \hspace{1cm} (14)

The derivatives $\partial \alpha_{\delta'}/\partial u_{\alpha, \alpha'}$ of the molecular polarizabil-
ities (in the crystal axes system) with respect to the ro-
tational displacements of the molecules (about the crys-
tal axes) are completely determined by the rotational
transformation properties of the molecular tensors $\alpha_{\delta'}'. So, for a given crystal structure the quantities $\Pi_{\alpha'}^{\alpha}$ can be calculated from the molecular polarizabilities $\alpha_{\delta}'$ and their rotational derivatives (both transformed to the
crystal axes system) and from the Lorentz tensors $L$.

D. Infrared intensities

A model for the infrared intensities of lattice vibra-
tions which is consistent with the description of the
Raman intensities\textsuperscript{11} (Sec. II C) has recently been pro-
posed.\textsuperscript{12} The integrated absorption intensity for phonon
mode $j$ measured with unpolarized radiation is

$$\Gamma_j = \frac{2\pi \hbar}{v c \omega_j (1 - \exp(-\beta \omega_j))} \sum_{\alpha} \left| \frac{\partial z_{\alpha}}{\partial Q_j} \right|^2,$$  \hspace{1cm} (16)

where $\partial z_{\alpha}/\partial Q_j$ is the dipole moment change induced in the
unit cell by the $(q = 0)$ mode with normal coordinate $Q_j$. This normal coordinate is composed of molecular
displacements; for ethylene only the translational dis-
placements $u'$ (the $u$ modes) are involved. For mole-
cules without intrinsic dipole moments (such as ethyl-
ene) a dipole moment can be induced by the interactions
with the neighbors according to the following three
mechanisms: polarization by the electric field of the
neighbors (and by external fields), dispersion forces,
and (short range) overlap effects. In compressed (pure)
gases it has been found\textsuperscript{21} that the first term yields the
main contribution to the collision induced IR absorp-
tion (although the overlap effects are nonnegligible; in gas
mixtures they are even dominant\textsuperscript{21-32}). Just as in our
model for the Raman intensities, we have neglected the
overlap and dispersion interactions. The remaining
polarization term yields the following (linear response)
expression\textsuperscript{12} for the dipole moment induced in a given
molecule $\alpha$ by the displacements $u'$ of other mole-
cules $\alpha''$

$$Z' = -\sum_{\alpha'} X_{\alpha\alpha'} \sum_{\nu} B_{\nu\alpha'} u'_{\nu \alpha'}.$$

The tensor $X_{\alpha\alpha'}$ is part of the electric susceptibility ten-
sor of the crystal including the local field corrections
[cf. Eq. (12)]

$$X_{\alpha\alpha'} = \frac{4 \pi}{v} (1 - \alpha \cdot L)_{\alpha, \alpha'}^{(-1)} \alpha_{\alpha'}$$

and $B_{\nu\alpha'}$ contains the derivatives of the electric field

TABLE II. Crystal structure of C₂D₄ space group P2₁/n (Z = 2).

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<th>Structure parameters</th>
<th>Lattice constants</th>
<th>Molecular orientations*</th>
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<th>Calculated (SCP)*</th>
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*By minimizing the internal energy (T = 0).
1By minimizing the free energy.
2Euler angles are defined as follows: Start with the molecule lying in the ac* plane, the C–C axis along the a axis, and rotate by t, η, and t about the a, b, and c* axes, respectively.

at site ' with respect to the displacements of the molecules ' in. In order to calculate the internal electric field in the crystal, the molecules can be represented by continuous charge distributions, by point multipoles, or by sets of point charges distributed over the molecules (not necessarily on the nuclei). We have chosen the latter representation, just as for the calculation of the electrostatic contribution to the crystal free energy and force constants (see Secs. II A and II B). Then, the field derivative matrix B takes the form

\[ B_{ab} = \sum_{n} q_{a}(m) \sum_{l} \varepsilon_{a}(l) \left| R_{a}(l) + R(l) \right|^{-1}, \]

where \( q_{a}(m) \) are the point charges placed on molecule ' at positions \( R(m) \) relative to the center of mass and the vectors \( R_{a}(l) \) are defined as in Eq. (4). The induced molecular dipole moments (17) can be summed over the unit cell and the dipole moment derivatives appearing in the infrared intensity (16) can be found by using the relation between the normal coordinates \( \delta_{ij} \) and the molecular displacements \( \vec{u}_{ij} \). Thus, we obtain

\[ \frac{\partial Z}{\partial Q_{j}} = \frac{\partial Z}{\partial \delta_{i}} \cdot B_{ij} \]

The susceptibility tensor \( \chi_{\alpha\beta} \) can be calculated as in Sec. II C from the molecular polarizabilities and the Lorentz tensor for the given crystal structure. For the same structure and a given set of molecular point charges (see Table I) the field derivatives \( B \) can be evaluated using Ewald’s method (which has been used also for the calculation of the Lorentz tensor). The eigenvectors \( e^{i}_{\alpha} \) are those from the lattice dynamics calculation again, but now for the translational \( q = 0 \) modes (the \( \theta \) modes).

III. RESULTS AND DISCUSSION

The results of the crystal structure optimization with the \( ab \) initio potential and with an empirical hydrocarbon potential (see Sec. II A) are shown in Table II. In the harmonic model calculation we have minimized the internal energy of the crystal (at \( T = 0 \)), neglecting the zero-point vibrations; in the SCP calculations we have minimized the Gibbs free energy for the temperatures and pressures where the experimental structure determinations were done. The overall agreement between the calculated and experimental data is fairly good, which is satisfactory especially for the \( ab \) initio potential since it contains no empirical fit parameters. In the SCP calculations (at zero pressure) the lattice appears to dilate relative to the harmonic calculation; this effect is mainly due to the zero-point motions. The largest relative increase occurs for the parameter \( b \) (which is smaller than the experimental value). The dilation is smaller for the \( ab \) initio potential, which is what one would expect since the empirical potential is somewhat softer (it yields lower phonon frequencies; see below). The lattice contraction which is obtained by increasing the pressure to 1.9 kbar is very well reproduced by the SCP calculations.

The phonon frequencies \( \omega_{j}(q) \) have been calculated for 312 wave vectors \( q \) in the fundamental wedge of the Brillouin zone, which is necessary for calculating the free energy (4) and the SCP effective force constants (5) via Eqs. (6) and (8). In Table III the results are shown just for \( q = 0 \), since only the optical frequencies have been measured so far. The agreement between calculations and experiment is reasonable, but somewhat less good than we have recently found for the N₂ crystal, where especially the translational mode frequencies were reproduced almost perfectly by the SCP treatment with an \( ab \) initio potential. This is probably due to the \( ab \) initio potential for C₂H₄ and, in particular, its analytic (atom–atom) representation, which has been obtained from fewer \( ab \) initio calculated points, being somewhat less accurate. (Moreover, the atom–atom model appeared to be more realistic for the N₂–N₂ potential than for the C₂H₄–C₂H₄ potential, in the short range region.)

In all cases, except for the lowest frequency \( B_{y} \) mode, the SCP anharmonic corrections lower the harmonic frequencies; the effective force constants are smaller than the second derivatives at the potential minimum. For the \( ab \) initio potential all SCP corrections improve the agreement with the experimental frequencies, i.e., they point in the right direction, but they are still considerably too small.
TABLE III. Optical (q = 0) phonon frequencies (cm\(^{-1}\)) in the C\(_2\)D\(_4\) crystal.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Empirical potential(^b)</th>
<th>(Ab\ ini) potential(^b)</th>
<th>(Ab\ ini) potential(^b)</th>
<th>Calculated (SCP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated (harmonic)</td>
<td>T = 30 K, (p = 0)</td>
<td>T = 99 K, (p = 1.9) kbar</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(B_1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A_1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(B_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A_3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(B_3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A_4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(B_4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)If these modes were assigned by their Raman intensities, their order would have to be reversed (only for the empirical potential; see Table V).

\(^b\)Measured at 20 K.\(^{3,4}\)

(If the potential is not completely realistic, they cannot, of course, fully remove the discrepancy.) For the empirical potential\(^b\) the SCP corrections actually make the results worse in some cases. This may be ascribed to the empirically fitted potentials containing already some effects of the anharmonic lattice vibrations implicitly. Increasing the pressure to 1.9 kbar raises all the phonon frequencies; changing the temperature in the range from 0 to 100 K has practically no effect (less than 1 cm\(^{-1}\)).

A result which is striking is that we have found practically no difference between the SCP eigenvectors \(e_i(q)\) and the harmonic ones, although the frequencies (the eigenvalues) do differ. So, for the calculations of the Raman and IR intensities we have used the eigenvectors from the harmonic calculations. The Raman intensities are shown in Tables IV and V for ethylene and deuterated ethylene, respectively. First, we observe from the difference between the absolute intensities in columns 4 and 5 of Table IV that the local field corrections to the crystal electric susceptibility\(^{11}\) are quite important. [Note that the Raman intensities depend on the fourth power of the matrix \((1 - \alpha \cdot \mathbf{L})^{-1}\); see Eqs. (14) and (15).] For the relative intensities, which is what can be reliably extracted from the measurements,\(^{25}\) the "oriented gas" model yields about the same results as the model which includes these corrections.

The relative intensities calculated with the \(ab\ ini\) potential agree reasonably well with experiment, except for the very low intensities of the two highest frequency modes in ethylene. These modes correspond with almost pure rotational oscillations of the C\(_2\)H\(_4\) molecules about their C-C axes (in phase, \(A_{e1}\); or out of phase, \(B_e\)). Since the proton mass is low, the amplitudes of these oscillations are relatively large. Apart from possible experimental inaccuracies in these low intensities, the SCP formalism and the model used for calculating the Raman intensities are probably less reliable in this case. For the corresponding modes in C\(_2\)D\(_4\) (see Table V) the agreement is much better.

The Raman intensities calculated with the empirical potential\(^b\) show an interesting discrepancy, both for C\(_2\)H\(_4\) and for C\(_2\)D\(_4\). If one were to assign the lowest two \(A_1\) modes by their intensities, rather than by their frequencies, then their order would be reversed. Look-

TABLE IV. Raman intensities of optical modes in the C\(_2\)H\(_4\) crystal.

<table>
<thead>
<tr>
<th>Mode symmetry</th>
<th>Empirical potential(^b)</th>
<th>(Ab\ ini) potential(^b)</th>
<th>(Ab\ ini) potential(^b)</th>
<th>Calculated (SCP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated (harmonic)</td>
<td>T = 30 K, (p = 0)</td>
<td>T = 99 K, (p = 1.9) kbar</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(B_1)</td>
<td>38 0.66</td>
<td>50 0.09</td>
<td>0.34</td>
<td>60 0.35</td>
</tr>
<tr>
<td>(A_1)</td>
<td>79 0.81</td>
<td>80 0.24</td>
<td>0.97</td>
<td>75 1.00</td>
</tr>
<tr>
<td>(A_2)</td>
<td>90 1.00</td>
<td>105 0.13</td>
<td>0.51</td>
<td>78 0.53</td>
</tr>
<tr>
<td>(B_2)</td>
<td>131 0.19</td>
<td>157 0.04</td>
<td>0.15</td>
<td>95 0.53</td>
</tr>
<tr>
<td>(A_3)</td>
<td>163 0.17</td>
<td>196 0.03</td>
<td>0.11</td>
<td>123 0.11</td>
</tr>
<tr>
<td>(B_3)</td>
<td>170 0.04</td>
<td>249 0.005</td>
<td>0.024</td>
<td>157 0.025</td>
</tr>
</tbody>
</table>

\(^a\)From the harmonic calculations (the eigenvectors are practically the same as the SCP eigenvectors).

\(^b\)Relative to the most intense mode.

\(^c\)In arbitrary units.
TABLE V. Raman intensities of optical modes in the C\textsubscript{2}D\textsubscript{4} crystal.

<table>
<thead>
<tr>
<th>Mode symmetry</th>
<th>Calculated\textsuperscript{a}</th>
<th>Empirical potential\textsuperscript{2}</th>
<th>Ab \textit{ab initio} potential\textsuperscript{b}</th>
<th>Experimental\textsuperscript{25}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Frequencies (cm\textsuperscript{-1})</td>
<td>Relative intensities\textsuperscript{b}</td>
<td>Frequencies (cm\textsuperscript{-1})</td>
<td>Relative intensities\textsuperscript{b}</td>
</tr>
<tr>
<td>B\textsubscript{1}</td>
<td>31</td>
<td>0.64</td>
<td>42</td>
<td>0.43</td>
</tr>
<tr>
<td>A\textsubscript{1}</td>
<td>66</td>
<td>0.66</td>
<td>67</td>
<td>1.00</td>
</tr>
<tr>
<td>A\textsubscript{2}</td>
<td>76</td>
<td>1.00</td>
<td>88</td>
<td>0.52</td>
</tr>
<tr>
<td>B\textsubscript{2}</td>
<td>111</td>
<td>0.20</td>
<td>134</td>
<td>0.13</td>
</tr>
<tr>
<td>A\textsubscript{1}</td>
<td>116</td>
<td>0.14</td>
<td>139</td>
<td>0.08</td>
</tr>
<tr>
<td>B\textsubscript{1}</td>
<td>121</td>
<td>0.014</td>
<td>176</td>
<td>0.015</td>
</tr>
</tbody>
</table>

\textsuperscript{a}From the harmonic calculations (the eigenvectors are practically the same as the SCP eigenvectors).
\textsuperscript{b}Relative to the most intense mode.

TABLE VI. Infrared intensities of optical modes in the C\textsubscript{2}H\textsubscript{4} crystal.

<table>
<thead>
<tr>
<th>Mode symmetry</th>
<th>Calculated\textsuperscript{a}</th>
<th>Empirical potential\textsuperscript{2}</th>
<th>Ab \textit{ab initio} potential\textsuperscript{b}</th>
<th>Experimental\textsuperscript{24}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Frequencies (cm\textsuperscript{-1})</td>
<td>Relative intensities\textsuperscript{b}</td>
<td>Frequencies (cm\textsuperscript{-1})</td>
<td>Relative intensities\textsuperscript{b}</td>
</tr>
<tr>
<td>A\textsubscript{1}</td>
<td>63</td>
<td>0.10</td>
<td>74</td>
<td>0.16</td>
</tr>
<tr>
<td>A\textsubscript{2}</td>
<td>75</td>
<td>0.33</td>
<td>93</td>
<td>0.72</td>
</tr>
<tr>
<td>B\textsubscript{1}</td>
<td>113</td>
<td>1.00</td>
<td>126</td>
<td>1.00</td>
</tr>
</tbody>
</table>

\textsuperscript{a}From the harmonic calculations (the eigenvectors are practically the same as the SCP eigenvectors).
\textsuperscript{b}Relative to the most intense mode.
frequencies is not consistent with their intensity ratio. So, this assignment may have to be reversed, but then the agreement with the measured frequencies is deteriorated.

The model[11] which we have used to calculate the Raman intensities in the ethylene crystal appeared to work quite well; the absolute intensities are strongly affected by the local field corrections, but the relative intensities practically do not change from the oriented gas results. The model for the IR intensities[12] has still to be improved, probably by taking the overlap induced dipole moments into account.

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