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

T. Luty,[b] A. van der Avoird, R. M. Berns, and T. Wasiutynski[c]

Institute of Theoretical Chemistry, University of Nijmegen, Toernooiveld, Nijmegen, The Netherlands
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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 anharmonic 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 type[1-3] (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,[6] 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 method[10] 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 crystals[11,12] 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 potentials[2,3] (a Buckingham exp-6 potential, supplemented with Coulombic interactions between

TABLE I. Parameters of the atom–atom potentials used for ethylene $(C_2H_4)^a$: $V(r_{ij}) = -A_{ij} r_{ij}^{-6} + B_{ij} \exp(-C_{ij} r_{ij}) + q_i q_j r_{ij}^{-1}$.

Parameters		*Ab initio* potential[6]	Empirical potential[2]
A	C–C	876	449.3
(kcal $\mathring{A}^6$ mol^{-1})	C–H	132	134.3
	H–H	20	40.15
B			
(kcal mol^{-1})	C–C	27 116	71 461
	C–H	6 368	14 316
	H–H	1 500	2 868
C	C–C	3.16	3.60
($\mathring{A}^{-1}$)	C–H	3.43	3.67
	H–H	3.70	3.74
q	C	-0.5274^b	-0.24
(unit charges)	H	$+0.2637^b$	$+0.12$

^{a}Atomic coordinates (in molecular frame): C: $(\pm 0.6685, 0.0, 0.0)$ Å, H: $(\pm 1.2335, \pm 0.9275, 0.0)$ Å.
^{b}"Atomic" charges shifted to positions: C': $(\pm 0.5549, 0.0, 0.0)$ Å, H': $(\pm 1.0095, \pm 0.8308, 0.0)$ Å.

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 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 initio* calculated multipole expansion coefficients).[8] The repulsive exponential terms represent the overlap interactions obtained from an *ab 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[8,9] and, since these would yield the dominant three-body contributions,[13,14] we can expect the ethylene crystal potential to have small deviations from pairwise (molecule–molecule) additivity[15,16] (a few percent of the binding energy at the van der Waals minimum).

The *ab initio* data[6] have been calculated for eight different orientations of the ethylene molecules and several intermolecular distances. For the long range r^{-n} 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 initio* potential is reasonably well represented. The parameters determining the analytical "*ab initio*" potential are collected in Table I, together with the parameters in a recent hydrocarbon atom–atom potential[2] fitted to the experimental data. In Ref. 6 we have seen that the most striking difference between the *ab initio* potential and various empirical hydrocarbon potentials[2,3] is that

the latter substantially underestimate the electrostatic multipole–multipole interactions between the C_2H_4 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.[10] The formalism starts from the following dynamical eigenvalue equations, just as the harmonic model:

$$D(q)e(q) = \omega^2(q) Me(q) , \tag{1}$$

where the tensor M contains the masses M^σ of the atoms in each sublattice σ:

$$M_{\alpha\beta}^{\sigma\sigma'} = M^\sigma \delta_{\sigma\sigma'} \delta_{\alpha\beta} \quad (\alpha, \beta = x, y, \text{ or } z) . \tag{2}$$

The eigenvalues $\omega_j(q)$ and eigenvectors $e_j(q)$ 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 ϕ:

$$D_{\alpha\beta}^{\sigma\sigma'}(q) = \sum_l \phi_{\alpha\beta}^{\sigma\sigma'}(l) \exp[iq \cdot R(l)] , \tag{3}$$

where the force constants are the second derivatives of the potential for the equilibrium structure of the crystal; $R(l)$ 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[10] 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:

$$F = \sum_{q,j} \{\beta^{-1} \ln[2 \sinh\tfrac{1}{2}\beta\omega_j(q)]$$
$$- \tfrac{1}{4}\omega_j(q) \coth\tfrac{1}{2}\beta\omega(q)\}$$
$$+ \tfrac{1}{2}N \sum_{R_{\sigma\sigma'}(l)} \langle V[R_{\sigma\sigma'}(l) + u_{\sigma\sigma'}(l)] \rangle . \tag{4}$$

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

$$\phi_{\alpha\beta}^{\sigma\sigma'}(l) = \langle \nabla_\alpha^\sigma \nabla_\beta^{\sigma'} V[R_{\sigma\sigma'}(l) + u_{\sigma\sigma'}(l)] \rangle . \tag{5}$$

This means that the second derivatives of the potential V have now to be averaged over the relative atomic displacements $u_{\sigma\sigma'}(l)$. 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 λ:

$$\langle Q[R_{\sigma\sigma'}(l) + u_{\sigma\sigma'}(l)]\rangle = (2\pi)^{-3/2}[\det(\lambda)]^{-1/2}$$

$$\times \int du\, Q[R_{\sigma\sigma'}(l) + u]\exp(-\tfrac{1}{2}u\lambda^{-1}u) . \qquad (6)$$

These functions λ are given by

$$\lambda_{\alpha\beta}(\sigma, \sigma', l) = \langle [u_{\sigma'}(l) - u_{\sigma}(0)]_{\alpha}[u_{\sigma'}(l) - u_{\sigma}(0)]_{\beta}\rangle \qquad (7)$$

and they can be calculated from the following expression:

$$\lambda_{\alpha\beta}(\sigma, \sigma', l) = \frac{\hbar}{cN}\sum_{q,j}[1 - \cos q \cdot R(l)]$$

$$\times \omega_j(q)^{-1}\coth\tfrac{1}{2}\beta\omega_j(q)\, e_j(q)_{\alpha}^{\sigma}e_j(q)_{\beta}^{\sigma'} , \qquad (8)$$

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.*[17] for the α 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[18] 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 $u^r = (\theta_x, \theta_y, \theta_z)$ of the (rigid) molecules; together these are grouped in a six-dimensional displacement vector $u = (u^t, u^r) = \{u_\alpha; \alpha = 1, \ldots, 6\}$. 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:

$$M_{\alpha\beta}^{\sigma} = 0 , \quad \text{for } \alpha = 4, 5, 6 \text{ and } \beta = 1, 2, 3$$

$$\text{and for } \alpha = 1, 2, 3 \text{ and } \beta = 4, 5, 6 , \qquad (9)$$

$$M_{\alpha\beta}^{\sigma} = I_{\alpha-3,\beta-3}^{\sigma} , \quad \text{for } \alpha = 4, 5, 6 \text{ and } \beta = 4, 5, 6 ,$$

where I^σ is the moment of inertia tensor of the molecules in the σ sublattice (in the crystal system of axes). The effective force constant matrix ϕ and its Fourier transform D have mixed translational–rotational (tr and rt) 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 λ^{tt}, λ^{tr}, λ^{rt}, and λ^{rr}.

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. IIA), 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 λ^{tt}, λ^{tr}, λ^{rt}, and λ^{rr} by substituting into Eq. (7) the following relation between atomic displacements $u(m)$ and the rigid molecule translations u^t and rotations u^r:

$$u(m) = u^t + u^r \times R(m) , \qquad (10)$$

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 $u^r = (\theta_x, \theta_y, \theta_z)$ are exact only for infinitesimal rotations u^r. So the SCP method, as generalized to molecular crystals by Wasiutynski,[18] may be less effective in correcting the harmonic model for larger amplitude anharmonic librations. Numerical calculations which have been carried out[19] on the ordered (α and γ) phases of solid N_2 (using an *ab initio* interaction potential[20] 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 hexamethylene tetramine crystal with one molecule in the primitive unit cell.[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,[21] using 3^3 and 5^3 points, respectively. Nondiagonal terms in the displacement–displacement correlation functions λ appear to be very small[18]; when evaluating expression (6), the off-diagonal terms in λ^{-1} have been neglected. The Helmholz 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 λ given by Eq. (8) transforms under symmetry operations in the same way as the force constant tensor ϕ [Eq. (5)], one can restrict the set of q to the fundamental wedge ($\tfrac{1}{4}$ of the Brillouin zone) and use the appropriate weight factors and transformation properties in the summations (4) and (8). In this wedge 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 crystal structure is known from x-ray diffraction,[22] but the monoclinic cell parameters a, b, c, and β and the Euler

angles ξ, η, ζ corresponding with the equilibrium orientations of the molecules have been optimized in the calculations (by minimizing the free energy as mentioned above). This minimization was carried out by the program package MINUITS.[23] The calculations have been made also for deuterated ethylene, for which the crystal structure under pressure is known.[24]

C. Raman intensities

In a sample of randomly oriented crystallites as one has for the Raman measurements on ethylene,[25] the polarized Stokes intensity for a nondegenerate lattice mode j with normal coordinate Q_j and frequency ω_j is given by[26]

$$I_j = \frac{\hbar \omega_s^4}{2\pi c^3 \omega_j [1 - \exp(-\beta\omega_j)]} \sum_{\alpha,\beta} \left| \frac{\partial \chi_{\alpha\beta}}{\partial Q_j} \right|^2 , \qquad (11)$$

where ω_s is the frequency of the scattered light $\omega_s = \omega_0 - \omega_j$. The tensor χ describes the (high frequency) electric susceptibility of the crystal. In the simplest ("oriented gas") model the molecules in the crystal are assumed to be noninteracting and the crystal susceptibility χ is given by the sum of the molecular polarizability tensors α^σ, expressed in the crystal principal axes system. Actually, the susceptibility χ which is the response function of the crystal to external electric fields is modified by the interactions between the molecules. 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 obtains[27]

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

where v is the unit cell volume, α is the $3n \times 3n$ tensor containing the molecular polarizability tensors $\alpha_{\sigma\sigma'} = \delta_{\sigma\sigma'} \alpha^\sigma$, L is the $3n \times 3n$ Lorentz tensor which is composed of 3×3 Lorentz tensors $L_{\sigma\sigma'}$,[27] and n is the number 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[28] 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[11]:

$$\frac{\partial \chi}{\partial Q_j} = \sum_\sigma \sum_\alpha \frac{\partial \chi}{\partial u^r_{\alpha,\sigma}} (e^r_j)^\sigma_\alpha , \qquad (13)$$

where $(e^r_j)^\sigma_\alpha$ are the (rotational) components ($\alpha = 4, 5, 6$) of the eigenvector for the librational mode j (with $q = 0$) which multiply the rotational displacements $u^r = (\theta_x, \theta_y, \theta_z)$ of the molecules σ. From Eq. (12), noting that the Lorentz tensors L do not change by rotational displacements (they depend only on the molecular positions), one finds, after some manipulation,[11]

$$\frac{\partial \chi}{\partial u^r_{\alpha,\sigma}} = \frac{4\pi}{v} \sum_{\sigma',\sigma''} (1 - \alpha \cdot L)^{-1}_{\sigma'\sigma} \frac{\partial \alpha^\sigma}{\partial u^r_{\alpha,\sigma}} (1 - L \cdot \alpha)^{-1}_{\sigma\sigma''} ,$$

$$= \Pi^\sigma_\alpha . \qquad (14)$$

The derivatives $\partial \alpha^\sigma / \partial u^r_{\alpha,\sigma}$ of the molecular polarizabilities (in the crystal axes system) with respect to the rotational displacements of the molecules (about the crystal axes) are completely determined by the rotational transformation properties of the molecular tensors α^σ. So, for a given crystal structure the quantities Π^σ_α can be calculated from the molecular polarizabilities α^σ and their rotational derivatives (both transformed to the crystal axes system) and from the Lorentz tensors L. From the lattice dynamics calculations (see Sec. II B) we have obtained the eigenvectors e^r_j and thus we can compute the intensity of the (unpolarized) Raman band for each mode j by the formula

$$I_j = \frac{\hbar \omega_s^4}{2\pi c^3 \omega_j [1 - \exp(-\beta\omega_j)]} \sum_{\alpha,\beta} \left| \sum_{\sigma,\gamma} (\Pi^\sigma_\gamma)_{\alpha\beta} (e^r_j)^\sigma_\gamma \right|^2 . \qquad (15)$$

The molecular polarizability of ethylene has been measured[29,30] and calculated by *ab initio* methods.[8] For the present calculations we have used the experimental values (which are not very different from the calculated ones): $\alpha_{xx} = 36.4$, $\alpha_{yy} = 26.1$, and $\alpha_{zz} = 22.9$ a.u., in a molecular frame with the x axis along the C–C bond and the molecule lying in the xy plane.

D. Infrared intensities

A model for the infrared intensities of lattice vibrations which is consistent with the description of the Raman intensities[11] (Sec. II C) has recently been proposed.[12] The integrated absorption intensity for phonon mode j measured with unpolarized radiation is

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

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 displacements u^t (the u modes) are involved. For molecules without intrinsic dipole moments (such as ethylene) 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[31] that the first term yields the main contribution to the collision induced IR absorption (although the overlap effects are nonnegligible; in gas mixtures they are even dominant[31-33]). 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[12] for the dipole moment induced in a given molecule σ by the displacements u^t of other molecules σ''

$$Z^\sigma = -\sum_{\sigma'} \chi_{\sigma\sigma'} \cdot \sum_{\sigma''} B_{\sigma'\sigma''} u^t_{\sigma''} . \qquad (17)$$

The tensor $\chi_{\sigma\sigma'}$ is part of the electric susceptibility tensor of the crystal including the local field corrections [cf. Eq. (12)]

$$\chi_{\sigma\sigma'} = \frac{4\pi}{v} (1 - \alpha \cdot L)^{-1}_{\sigma\sigma'} \cdot \alpha^{\sigma'} \qquad (18)$$

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

TABLE II. Crystal structure of C_2D_4 space group $P2_1/n$ $(Z = 2)$.

Structure parameters		Calculated (harmonic)[a]		Calculated (SCP)[b] $T = 85$ K, $p = 0$			Calculated (SCP)[b] $T = 99$ K, $p = 1.9$ kbar		
		Empirical potential[2]	*Ab initio* potential[6]	Empirical potential[2]	*Ab initio* potential[6]	Experimental[24]	Empirical potential[2]	*Ab initio* potential[6]	Experimental[24]
Lattice constants	a(Å)	4.726	4.730	4.799	4.782	4.613	4.716	4.710	4.506
	b(Å)	6.435	6.205	6.610	6.334	6.610	6.546	6.280	6.558
	c(Å)	4.135	4.004	4.212	4.064	4.037	4.121	4.000	3.977
	β(deg)	93.9	88.5	93.4	88.2	94.5	94.2	89.1	95.2
Molecular orientations[c]	ξ(deg)	−27.0	−31.7	−27.8	−32.2	−27.0	−28.2	−32.0	−26.8
	η(deg)	−11.7	−9.3	−11.2	−9.1	−14.6	−11.6	−9.4	−14.2
	ζ(deg)	−31.8	−31.3	−32.0	−31.5	−34.3	−31.9	−31.6	−34.3

[a]By minimizing the internal energy $(T = 0)$.
[b]By minimizing the free energy.
[c]Euler 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 ξ, η, and ζ about the a, b, and c^* axes, respectively.

at site σ' with respect to the displacements of the molecules σ''. 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

$$B_{\alpha\beta}^{\sigma\sigma'} = \sum_{m\in\sigma'} q_{\sigma'}(m) \sum_l \nabla_\alpha \nabla_\beta \left| R_{\sigma\sigma'}(l) + R(m) \right|^{-1}, \quad (19)$$

where $q_{\sigma'}(m)$ are the point charges placed on molecule σ' at positions $R(m)$ relative to the center of mass and the vectors $R_{\sigma\sigma'}(l)$ 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 Q_j and the molecular displacements u_σ^t. Thus, we obtain

$$\frac{\partial Z}{\partial Q_j} = \sum_\sigma \frac{\partial Z^\sigma}{\partial Q_j} = \sum_\sigma \sum_{\sigma',\alpha} \frac{\partial Z^\sigma}{\partial u_{\alpha,\sigma'}^t} (e_j^t)_\alpha^{\sigma'}$$

$$= -\sum_{\sigma,\sigma',\sigma''} \chi_{\sigma\sigma''} \cdot B_{\sigma''\sigma'} \cdot (e_j^t)^{\sigma'}. \quad (20)$$

The susceptibility tensor $\chi_{\sigma\sigma'}$ 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[26] (which has been used also for the calculation of the Lorentz tensor). The eigenvectors e_j^t are those from the lattice dynamics calculation again, but now for the translational $q = 0$ modes (the u modes).

III. RESULTS AND DISCUSSION

The results of the crystal structure optimization with the *ab initio* potential and with an empirical hydrocarbon potential[2] (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[24] 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.[25,34] The agreement between calculations and experiment is reasonable, but somewhat less good than we have recently found[19] for the N_2 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 C_2H_4 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 N_2–N_2 potential than for the C_2H_4–C_2H_4 potential, in the short range region.)

In all cases, except for the lowest frequency B_g 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_2D_4 crystal.

		Calculated (harmonic)		Calculated (SCP)			Calculated (SCP)
				$T=30$ K, $p=0$			$T=99$ K, $p=1.9$ kbar
Symmetry		Empirical potential[2]	*Ab initio* potential[6]	Empirical potential[2]	*Ab initio* potential[6]	Experimental[25,34]	*Ab initio* potential[6]
Librational modes	B_g	31.1	41.6	33.4	42.6	60	44.6
	A_g	65.7[a]	66.9	64.8[a]	66.6	75	74.1
	A_g	76.3[a]	87.6	74.3[a]	84.6	78	90.2
	B_g	111.1	134.5	107.2	130.3	95	139.4
	A_g	116.3	139.5	111.7	136.0	123	146.5
	B_g	120.7	176.3	118.2	172.7	135	181.4
Translational modes	A_u	59.1	69.9	54.9	66.6	...	73.1
	A_u	69.9	87.7	65.6	83.2	69.5[b]	89.0
	B_u	105.2	118.3	99.2	113.4	104.0[b]	124.8

[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.[34]

(If the potential is not completely realistic, they cannot, of course, fully remove the discrepancy.) For the empirical potential[2] the SCP corrections actually make the results worse in some cases. This must probably 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 $e_j(q)$ 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 $(1 - \alpha \cdot L)^{-1}$; 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 initio* 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_2H_4 molecules about their C–C axes (in phase, A_g, or out of phase, B_g). 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_2D_4 (see Table V) the agreement is much better.

The Raman intensities calculated with the empirical potential[2] show an interesting discrepancy, both for C_2H_4 and for C_2D_4. If one were to assign the lowest two A_g 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_2H_4 crystal.

			Calculated[a]				Experimental[25]	
	Empirical potential[2]			*Ab initio* potential[6]				
					Absolute intensities[c]			
Mode symmetry	Frequencies (cm^{-1})	Relative intensities[b]	Frequencies (cm^{-1})	Oriented gas model	With local field corrections	Relative intensities[b]	Frequencies (cm^{-1})	Relative intensities[b]
B_g	38	0.66	50	0.09	0.34	0.35	73	0.19
A_g	79	0.81	80	0.24	0.97	1.00	90	1.00
A_g	90	1.00	105	0.13	0.51	0.53	97	0.42
B_g	131	0.19	157	0.04	0.15	0.15	114	0.20
A_g	163	0.17	196	0.03	0.11	0.11	167	0.006
B_g	170	0.04	249	0.005	0.024	0.025	177	0.002

[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_2D_4 crystal.

	Calculated[a]				Experimental[25]	
	Empirical potential[2]		*Ab initio* potential[6]			
Mode symmetry	Frequencies (cm^{-1})	Relative intensities[b]	Frequencies (cm^{-1})	Relative intensities[b]	Frequencies (cm^{-1})	Relative intensities[b]
B_g	31	0.64	42	0.43	60	0.17
A_g	66	0.66	67	1.00	75	1.00
A_g	76	1.00	88	0.52	78	0.50
B_g	111	0.20	134	0.13	95	0.20
A_g	116	0.14	139	0.08	123	0.08
B_g	121	0.014	176	0.015	135	0.013

[a]From the harmonic calculations (the eigenvectors are practically the same as the SCP eigenvectors).
[b]Relative to the most intense mode.

ing at the frequencies alone, one could not detect such a discrepancy and the danger of trying to improve the empirical fit parameters by using the measured phonon frequencies[3] is clearly demonstrated here. Also, the overall agreement with the measured relative Raman intensities is less good for the empirical potential than it is for the *ab initio* potential.

Table VI shows that the agreement between the calculated relative IR intensities and the measured data[34] is rather bad, both for the *ab initio* potential and for the empirical one; the latter seems to give slightly worse results. Maybe the ethylene films on which the IR intensity measurements have been made do not correspond with the model of randomly oriented crystallites for which formula (16) has been derived. Due to the symmetry, the induced dipole moment must lie along the crystal b axis for the A_u modes, while it follows from the calculations that the B_u mode yields a dipole transition moment nearly parallel to the a axis. A comparison with polarized IR spectra would be very informative. On the other hand, the model used for calculating the induced dipole moments is probably too crude. In particular, the neglect of overlap effects on the induced dipoles may lead to inaccuracies. The reason why the calculated IR intensities are worse than the Raman intensities could be that the latter appear already in the oriented gas model, i.e., they depend in the first instance just on the molecular polarizability tensors (in particular, on their rotational transformation behavior). A result which seems to be consistent with experiment is that the lowest frequency A_u mode, which has not been

observed until now, is indeed calculated to have a low relative intensity.

IV. CONCLUSIONS

Summarizing the discussions, we conclude that the intermolecular C_2H_4 potential from *ab initio* calculations[6-9] yields a fairly good structure and reasonably good phonon frequencies for the ethylene crystal. If the anharmonic effects are taken into account by the self-consistent phonon method, the frequencies are systematically improved; the corrections are substantially too small to yield agreement with experiment, however. The effects of pressure on the ethylene crystal structure and on the phonon frequencies are well represented by the SCP calculations. From the calculation of the (relative) intensities of the Raman active optical modes it was found that the calculated polarization vectors of these modes are fairly realistic, too.

An empirical hydrocarbon atom–atom potential[2] also yields a fairly good crystal structure and reasonably good phonon frequencies, but now the harmonic frequencies are not always improved by the SCP corrections. This might be expected since the empirical potential probably contains the effects of the (anharmonic) lattice vibrations implicitly already; so, the results will not be improved by again adding these effects explicitly. The polarization vectors obtained from this empirical potential are less realistic, as shown by the comparison of the Raman intensities. In particular, it was found in this case that the assignment of two A_g modes by their

TABLE VI. Infrared intensities of optical modes in the C_2H_4 crystal.

	Calculated[a]				Experimental[34]	
	Empirical potential[2]		*Ab initio* potential[6]			
Mode symmetry	Frequencies (cm^{-1})	Relative intensities[b]	Frequencies (cm^{-1})	Relative intensities[b]	Frequencies (cm^{-1})	Relative intensities[b]
A_u	63	0.10	74	0.16	···	···
A_u	75	0.33	93	0.72	73	1.00
B_u	113	1.00	126	1.00	110	0.66

[a]From the harmonic calculations (the eigenvectors are practically the same as the SCP eigenvectors).
[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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