

## Phonons of the *cis*-polyacetylene chain

Eric Faulques, Jean-Pierre Buisson, and Serge Lefrant

Laboratoire de Physique Cristalline, Institut des Matériaux de Nantes, 2 rue de la Houssinière, F-44072 Nantes, France

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An investigation of the in-plane phonons of the *cis*-polyacetylene chain  $(\text{CH})_x$  and isotopic analogs  $(\text{CD})_x$  and  $(^{13}\text{CH})_x$  is presented on the basis of a Fourier's dynamical  $D$ -matrix formalism. The conjugation is found to be similar to that of the *trans*-polyacetylene chain. Phonon dispersions have been calculated and follow the shapes predicted by Božović. Finally, the most interesting result is that phonon density of states exhibits van Hove singularities whose energies are close to those determined experimentally with incoherent inelastic neutron scattering.

Polyacetylene  $(\text{CH})_x$  has received great interest since the two past decades because this polymer is the basic example of synthetic metals reaching quasimetallic conductivity values when doped with electron donors or acceptors.<sup>1</sup> These conducting properties are closely related to the conjugation of the carbon-carbon bonds along the polymeric chain. The polymer exists as isomers *cis* and *trans*, the former being the less stable.  $(\text{CH})_x$  is an ideal model compound for the study of possible nonlinear collective excitations of the electronic system such as solitons and polarons<sup>2</sup> for which there is a large body of evidence. These quasiparticles are believed to travel along the  $z$  axis of the chain by breaking the  $\pi$ -electron conjugation. Relevant information about the electronic structure and force constants of polyacetylene were given by Raman and IR spectroscopy for which vibrational models have been derived particularly in the case of *trans*-polyacetylene.<sup>3</sup> In this paper we present a theoretical study of the in-plane phonons of the *cis*-polyacetylene chain for  $0 \leq q \leq \pi/a$ . Rakovic and co-workers initiated the first comparative study of the vibrations in *trans*- and *cis*-polyacetylene<sup>4-6</sup> at  $q=0$ , but hereafter we give the main frame of our model and describe the extent to which it differs from the *trans*-polyacetylene calculation. Moreover, incoherent inelastic neutron-scattering data obtained at ILL of Grenoble<sup>7</sup> on oriented crystalline *cis*-polyacetylene have attracted our attention recently because they provided an opportunity to compare our theoretical model at  $q \neq 0$  with experiment.

The method for calculating the chain phonons can be described as follows. The phonon frequencies  $\omega$  are obtained by solving the eigenvalue problem  $|D(\mathbf{q}) - I\omega(\mathbf{q})^2| = 0$ , where  $D$  is the dynamical Fourier matrix and  $\mathbf{q}$  is the wave vector. This method has a mathematical advantage<sup>3,8</sup> over the usual  $GF$ -matrix solution of Wilson *et al.*<sup>9</sup> The  $D$  matrix is Hermitian and thus symmetric and is easily diagonalized by blocks, whereas the  $GF$  matrix is not symmetric and leads to oversized calculations. The  $D$  matrix is expressed in Cartesian coordinates as  $D(\mathbf{q}) = M^{1/2} B_{0p}^T(\mathbf{q}) F_{0p}^T(\mathbf{q}) B_{0p}(\mathbf{q}) M^{1/2}$ , where  $M$  is the matrix of atomic masses,  $F_{0p}^i$  is the force constant matrix expressed in internal coordinates, and  $B_{0p}$  is a matrix changing the internal coordinates to Cartesian coordinates. The interactions are chosen by considering a two-body potential and a valence force field. The initial force constants are transferred from *ab initio* calculations on short polyenes and then refined to match the observed

frequencies.<sup>3</sup> The  $F_{0p}^i$  matrix of the one-dimensional (1D) crystal is defined in the same manner as Shimanouchi *et al.*<sup>10</sup> and Piseri and Zerbi<sup>11</sup> by considering only the first-neighbor cells. If we set the cell 0 for origin, we have  $F_{0p}^i = F_{-1}^i e^{-iqa} + F_0^i + F_1^i e^{iqa}$ , where  $F_{-1}^i, F_0^i, F_1^i$  are the force constant matrices of the cells labeled  $-1$  (first neighbor,  $-z$  direction),  $0$  (origin cell),  $+1$  ( $+z$  direction). Similarly we define  $B_{0p} = B_{-1} e^{-iqa} + B_0 + B_1 e^{iqa}$ . The bond lengths of the unit cell of *cis*- $(\text{CH})_x$  we have introduced in the  $B$  matrix are  $l\text{-C}=\text{C}=1.36 \text{ \AA}$ ,  $l\text{-C}-\text{C}=1.46 \text{ \AA}$ ,  $l\text{-C}-\text{H}=1.08 \text{ \AA}$ , with a cell parameter  $a=4.16 \text{ \AA}$ . For simplicity, angles are set equal to  $120^\circ$ . The polymeric chain is planar, which allows decoupling of in-plane and out-of-plane modes. The vibrational spectra<sup>12,13</sup> of *cis*- $(\text{CH})_x$  and isotopic analog polymers  $(^{13}\text{CH})_x$  and  $(\text{CD})_x$  are considered simultaneously to ascribe the vibrational modes with the help of Teller-Redlich rules. The vibrational spectrum is simulated by calculating the full phonon density of states,  $g(\omega) = \sum_q \sum_j \delta(\omega_{qj} - \omega)$ , where  $\omega_{qj}$  is the frequency of branch  $j$ . For a 1D chain with  $n$  atoms per unit cell and  $N$  primitive cells, we have  $3nN$  frequencies and

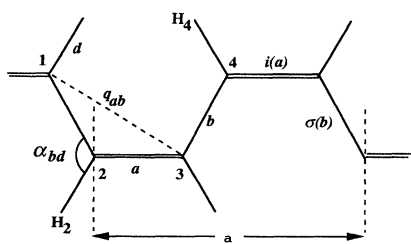
$$g(\omega) = \lim_{\Delta\omega \rightarrow 0} \frac{1}{3nN(\Delta\omega)} \frac{Na}{2\pi} \sum_j \int_{\omega \leq \omega_j(q) \leq \omega + \Delta\omega} \Delta q.$$

Since  $\Delta q = \Delta\omega / |d\omega_j/dq|$ , the 1D phonon density of states for  $q > 0$  and in-plane modes is expressed as

$$g(\omega) = \frac{a}{4n\pi} \sum_j \frac{1}{|\text{grad}\omega_j(\mathbf{q})|},$$

with  $n=8$  in *cis*- $(\text{CH})_x$ . We calculate the Raman intensities at  $q=0$  by projecting the phonon density of states onto C=C bonds since the stretching  $E$  motions of the  $\pi$  bonds modulate the electronic polarizability responsible for the Raman effect. Note that out-of-plane modes give vibrations perpendicular to the chain plane and thus weakly modulate the  $\pi$ -electron system, which means that their contribution to the Raman intensity is negligible. The intensity of the Raman modes is estimated from the projected density of states,

$$g_E(\omega) = \sum_l \langle E | V_0^l \rangle \langle V_0^l | E \rangle \delta(\omega_{0l} - \omega),$$

FIG. 1. Internal coordinates of a  $cis-(CH)_x$  chain.

where  $|V_0^l\rangle$  is the eigenvector of the  $l$  branch for  $q=0$ . The carbon atoms of the backbone cell  $C-C=C-C$  are labeled 1, 2, 3, 4 and 32 internal coordinates have been defined upon action of symmetry operations  $i$  and  $\sigma_{xy}$ . Coordinates  $a$ ,  $b$ , and  $d$  refer, respectively, to  $C=C$ ,  $C-C$ , and  $C-H$  bonds;  $q_{ab}$ ,  $q_{ad}$ , and  $q_{bd}$  describe coordinates between nonbonded atoms:  $C_1-C_3$ ,  $H_2-C_3$ , and  $H_4-C_3$ ,  $H_2$  and  $H_4$  being linked to  $C_2$  and  $C_4$ , respectively;  $\alpha_{ad}$  and  $\alpha_{ab}$  are the variations of  $H-C=C$  and  $C-C=C$  angles (Fig. 1). The dynamical matrix  $F_{0p}^i$  restricted to the couplings of the carbon skeleton is computed in Table I. The force constants defined for stretching, bending, and central forces are  $K(\alpha^2)\cdots K(\alpha_{ab}^2)\cdots K(q_{ab}^2)\cdots$ . First- and second-neighbor couplings are added between adjacent or nonadjacent carbon-carbon bonds;  $K(ab)$ ,  $K(bb)$ ,  $K(aa)$ , and between bonds adjacent to angles,  $K(\alpha_{ab},b)\cdots$ . These interactions are listed in Table II.

The in-plane zone center vibrations are represented by  $\Gamma(0)=4A_0^++4A_1^++3A_0^-+3A_1^-$  and  $\Gamma(\pi/a)=8E_{A_0}^{A_1}$  (line group  $L2_1/mcm$ ), while we have  $\Gamma(q)=8A_0+8A_1$  in the Brillouin zone (star group  $L2_1mc$ ). Here we use the notation of Božović and Vujicic for line group representations<sup>14</sup> corresponding at  $q=0$  to  $A_g, B_{2g}, B_{1u}$ , and  $B_{3u}$ , respectively, for point group  $D_{2h}$ . In the chain plane the compatibility relations are  $(A_0^+, A_0^-) \rightarrow A_0 \rightarrow E_{A_0}^{A_1}$  and  $(A_1^+, A_1^-) \rightarrow A_1 \rightarrow E_{A_0}^{A_1}$ . In the calculation the Teller-Redlich rules could not be completely fulfilled because some  $A_1^+$  experimental modes were lacking. The overall classification of the modes we have adopted is in accordance with measurements of Tubino.<sup>15</sup> Table III compares the experimental frequencies<sup>12</sup> determined in our group with the present calculation. For the three polymers the deviation with experiment is better than 2%

TABLE II. Refined force constants (units in  $\text{mdyn } \text{\AA}^{-1}$ ,  $\text{mdyn } \text{\AA}$ ;  $\text{mdyn } \text{\AA} \text{ rad}^{-2}$ ).

Interaction	$Cis\text{-hexatriene}^a$	$Cis\text{-(CH)}_x^b$	$Cis\text{-(CH)}_x$ this work <sup>c</sup>
$K(a^2)$	7.45	6.70	6.04
$K(b^2)$	5.16	3.87	3.79
$K(d^2)$	5.02	5.05	4.86
$K(\alpha_{ab}^2)$	0.83	0.80	0.46
$K(\alpha_{bd}^2)$	0.37	1.00	0.66
$K(\alpha_{ad}^2)$	0.41	1.00	0.60
$K(ab)$	0.22	0.95	0.30
$K(bb)$	-0.018	0.18	1.10
$K(aa)$	-0.55	0.63	0.96
$K(\alpha_{ab},b)$	0.19	-0.29	0.35
$K(\alpha_{bd},b)$	0.24	0.27	0.54
$K(\alpha_{bd},d)$	0.39		-0.44
$K(\alpha_{ad},d)$	0.23		0.57
$K(\alpha_{ad},a)$	0.34	0.59	0.36
$K(\alpha_{ab},a)$	0.67	-0.51	0.79
$K(q_{ab}^2)$			0.
$K(q_{bd}^2)$			0.01
$K(q_{ad}^2)$			0.03
conjugation	0.180	0.267	0.228

<sup>a</sup>Reference 17.<sup>b</sup>Reference 16.<sup>c</sup>This work.

except for the first  $A_1^-$  mode of  $(CH)_x$ , which has been found theoretically at  $1032 \text{ cm}^{-1}$  and at  $1115 \text{ cm}^{-1}$  experimentally, whereas in  $(CD)_x$  there is no such discrepancy. The assignment of the  $1115\text{-cm}^{-1}$  mode of  $(CH)_x$  in the  $A_1^-$  representation is certainly not correct either because it is an out-of-plane vibration or a remnant contribution of a  $trans\text{-(CH)}_x$  Raman mode<sup>3</sup> induced by partial isomerization and located near  $1100 \text{ cm}^{-1}$ . The experimental  $A_0^+$  lines are located at  $910, 1250, 1540,$  and  $3090 \text{ cm}^{-1}$ , and they are the strongest Raman modes. We got good agreement for three of them, but the  $1540\text{-cm}^{-1}$  line was calculated at  $1510 \text{ cm}^{-1}$  with a discrepancy of 3%. The  $A_0^+$  lines calculated at  $905$  and  $1249 \text{ cm}^{-1}$  arise from intermixing of  $C-C$  and  $C=C$  bendings, the one at  $1510 \text{ cm}^{-1}$  mainly stems from a  $C=C$  stretch, and the mode at  $3107 \text{ cm}^{-1}$  is the  $C-H$  stretch. In  $trans\text{-(CH)}_x$  we found two possible sets (I and II) of force constants

TABLE I. Dynamical  $F_{0p}^i$  matrix of  $cis\text{-(CH)}_x$  (upper rows) and  $trans\text{-(CH)}_x$  (the two lower rows) in internal coordinates restricted to carbon-carbon stretchings.  $i(a)$  and  $\sigma_{xy}(b)$  are the internal coordinates resulting from action of inversion and mirror operations on  $a$  and  $b$  ( $z$  is the chain axis;  $x$  is normal to the plane).

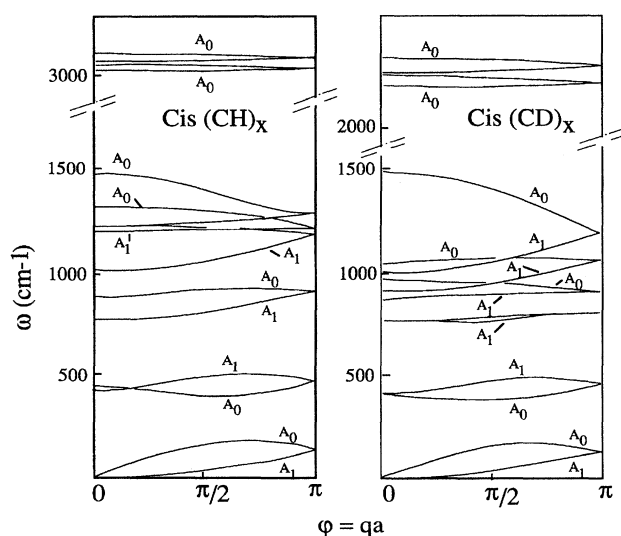
$a$	$b$	$i(a)$	$\sigma_{xy}(b)$	
$K(a^2)$	$K(ab)$	$K(aa)(1+e^{-iqa})$	$K(ab)e^{-iqa}$	$a$
$K(ab)$	$K(b^2)$	$K(ab)$	$K(bb)(1+e^{-iqa})$	$b$
$K(aa)(1+e^{iqa})$	$K(ab)$	$K(a^2)$	$K(ab)$	$i(a)$
$K(ab)e^{iqa}$	$K(bb)(1+e^{iqa})$	$K(ab)$	$K(b^2)$	$\sigma_{xy}(b)$
$K(a^2)+2K(aa)\cos qa$	$K(ab)(1+e^{-iqa})$			$a$
$K(ab)(1+e^{iqa})$	$K(b^2)+2K(bb)\cos qa$			$b$

TABLE III. Experimental and calculated optical zone center frequencies (in  $\text{cm}^{-1}$ ).

Symmetry	$(\text{CH})_x$		$(\text{CD})_x$		$(^{13}\text{CH})_x$	
	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.
$A_0^+$	910	905	766	774	877	877
	1250	1249	975	977	1228	1242
	1540	1510	1476	1497	1499	1453
	3090	3107	2315	2342		3093
$A_1^+$	446	434	403	414		419
	828	797		769	812	768
		1250		917		1247
	3030	3067	2260	2271		3057
$A_0^-$	445	443	402	405	435	429
	1330	1343	1050	1047	1320	1333
	3044	3025	2255	2203	3030	3018
	1115	1032	892	886		993
$A_1^-$	1247	1233	947	1010	1200	1232
	3055	3055	2275	2253	3047	3045

(FC's) involving the  $a$  and  $b$  internal coordinates<sup>3</sup> because the pairs  $[K(a^2), K(aa)]$  and  $[K(b^2), K(bb)]$  were not separated in the  $F$  matrix (Table I) at the zone center. This interdependence is due to the structural degeneracy of  $\text{trans}(\text{CH})_x$  where C—C and C=C bonds may be exchanged without consequence to the ground-state energy. The lowest  $\pi$ -electron localization was given by set I with  $K(a^2)=5.42$  mdyn  $\text{\AA}^{-1}$ ,  $K(b^2)=3.4$  mdyn  $\text{\AA}^{-1}$ ,  $K(aa)=-0.46$  mdyn  $\text{\AA}^{-1}$ , and  $K(bb)=-0.10$  mdyn  $\text{\AA}^{-1}$ . In the case of  $\text{cis}(\text{CH})_x$ , there is separation of force constants at the zone center because the backbone structure is not degenerate; exchanging C—C and C=C bonds leads to different ground states. We find a unique set of possible interactions with  $K(a^2)=6.04$  mdyn  $\text{\AA}^{-1}$  and  $K(b^2)=3.79$  mdyn  $\text{\AA}^{-1}$ . The conjugation degree of the backbone chain defined as  $[K(a^2)-K(b^2)]/[K(a^2)+K(b^2)]$  is the same as in  $\text{trans}(\text{CH})_x$  (23%) even though the FC's taken separately are not the same in the two polymers. Our force constant values

seem realistic partly because they are close to the previous calculation of Benoit *et al.*<sup>16</sup> who have considered carbon-carbon interactions up to the third neighbor. However, the FC  $K(a^2)$  characterizing the C=C stretching has a lower value in the present work, whereas the other stretching FC's have rather similar values. In  $\text{cis}$ -hexatriene, for instance, the stretching FC's of the polymer backbone have higher values because the  $\pi$  electrons are less delocalized due to the finite size of this molecule.<sup>17</sup> Phonon dispersion curves of  $(\text{CH})_x$  and  $(\text{CD})_x$  have been calculated (Fig. 2).  $\text{cis}(\text{CH})_x$  belongs to a nonsymmorphic line group since it has a screw chain axis. Therefore, considering that the characters of the irreducible representations<sup>14</sup> are  $\chi=\pm\exp(iqta)$  and  $\chi'=\pm\exp[iq(t+1/2)a]$  for  $0<q<\pi/a$ , it is easy to label each branch with  $A_0$  and  $A_1$  representations. The branches of different symmetry can cross each other while at the zone boundary  $q=\pi/a$ , the irreducible representations are bidimensional, and these branches stick together. Dispersions show that the modes which are the most dependent on the lattice are associated with the C=C stretching, namely, the  $A_0^+$  mode at  $1510$   $\text{cm}^{-1}$  and the  $A_1^-$  mode at  $1032$   $\text{cm}^{-1}$  in  $(\text{CH})_x$ . For  $(\text{CD})_x$  the dispersion is much stronger for the  $1497$ - $\text{cm}^{-1}$   $A_0^+$  mode and similar to  $(\text{CH})_x$  for the modes at  $1010$   $\text{cm}^{-1}$  ( $A_1^-$ ) and  $917$   $\text{cm}^{-1}$  ( $A_1^+$ ). We notice that inside the first Brillouin zone the  $A_0$  modes soften, whereas the  $A_1$  modes harden (respectively,  $A_0^+$ ,  $A_0^-$  and  $A_1^+$ ,  $A_1^-$  at the zone center) contrary to the case of  $\text{trans}(\text{CH})_x$  where all modes harden between  $\Gamma$  and Z points. This is in agreement with the semiloop band shape predicted by Božović in polymers containing a glide plane.<sup>18</sup>  $\text{Trans}(\text{CH})_x$  has a lower symmetry ( $L_{1m}$ ) and thus presents only simple line or semicross band shapes. In Ref. 16 the dispersions are more spaced and do not mix since it was considered that the modes calculated at  $1575$  and  $1423$   $\text{cm}^{-1}$  (deuterated form) should correspond to experimental lines at  $1170$   $\text{cm}^{-1}$ ; dispersion mixing is avoided by introducing this discrepancy with experiment. Note also that the transverse acoustic mode has a zero slope at the  $\Gamma$  point which yields zero sound velocity. This is explained by the quadratic dependence of  $q$  with  $\omega$  in the 1D

FIG. 2. Phonon dispersion curves of  $\text{cis}(\text{CH})_x$  and  $\text{cis}(\text{CD})_x$ .

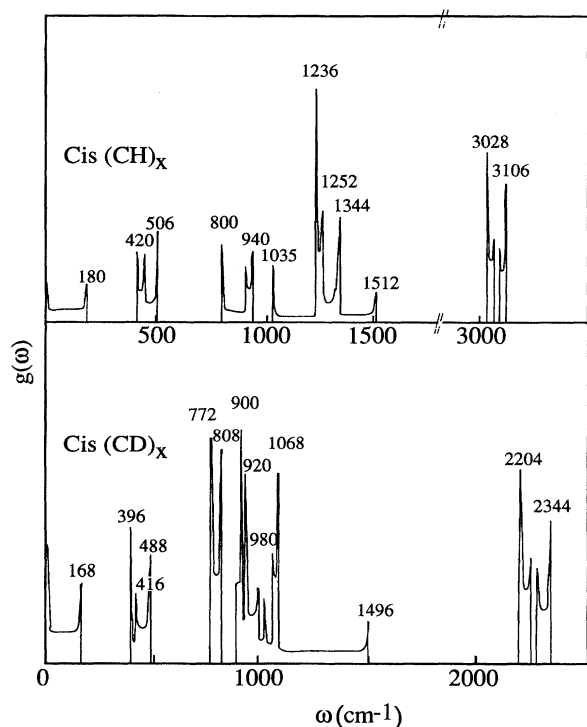


FIG. 3. Phonon density of states of *cis*-(CH)<sub>x</sub> and *cis*-(CD)<sub>x</sub>.

model. The phonon densities of states (PDOS) are presented in Fig. 3. The peaks are critical points and correspond to the vanishing component of  $\text{grad } \omega_{qj}$  in the phonon dispersion curves. This is a means to check the dispersions as well. We find 12 peaks for (CH)<sub>x</sub>, which is fewer than calculated in Ref. 16. The inelastic neutron-scattering spectra on *cis*-(CH)<sub>x</sub>-oriented films<sup>7</sup> determined by Sauvajol *et al.* show that the experimental frequency distribution  $g(\omega)$  exhibits several strong peaks at 250, 427, 968, 1210, and 1370 cm<sup>-1</sup>,

which are close to the present ones calculated, respectively, at 180, 420, 940, 1236, and 1344 cm<sup>-1</sup>. The envelopes of the full vibrational spectrum including IR and Raman  $q=0$  modes actually map the experimental  $g(\omega)$ . The set of three singularities at 420, 443, and 506 cm<sup>-1</sup> appears as a weak neutron-scattering contribution. The gap between 500 and 800 cm<sup>-1</sup> is well reproduced in the experiment; the regions of strong  $g(\omega)$  between 800 and 1050 cm<sup>-1</sup> (for  $Q_{\perp}$ ) and 1200 and 1500 cm<sup>-1</sup> (for  $Q_{\parallel}$ ) correspond to peak clusters of the calculation. This gives strong support to the choice of the force constant set in our model. Note, however, that our PDOS does not show the experimental peaks at 23, 50, 116, 250, and 312 cm<sup>-1</sup>. This is not surprising since these modes are 3D lattice phonons which cannot be reproduced in our 1D calculation. For example, the strong experimental peak at 2.9 meV (23 cm<sup>-1</sup>) is attributed by Sauvajol *et al.* to a damped translational mode whose energy may be strongly dependent on the interchain interactions. Then this peak results directly from a 3D coupling. Finally, in order to get insight about the Raman intensities, we have calculated the projected density of phonon states  $g_E(\omega)$  at the zone center onto the C=C bonds. The relative Raman intensities are, respectively, 2.3, 2.6, and 1 for the lines at 910, 1250, and 1540 cm<sup>-1</sup> in spectra of *cis*-(CH)<sub>x</sub> recorded at 600 nm excitation, where long chains are in resonance with absorption, whereas the calculated intensities  $\rho_E(\omega) = g_E(\omega)/g_E(1510)$  for these modes amounts to 0.16, 0.1, and 1.

In summary, the conjugation in *cis*-(CH)<sub>x</sub> is found to be the same as that of *trans*-(CH)<sub>x</sub>. The force constant set describes well the observed phonon density of states from inelastic neutron scattering in this polymer. A more sophisticated model including chain-length disorder, electron-phonon coupling, long-range effects, and transition dipole moments should be developed to account for the Raman intensities.<sup>13,19,20</sup>

The Institut des Matériaux de Nantes is "Unité Mixte de Recherche No. 110 CNRS-Université de Nantes."

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