

## Spectroscopic Studies on Ethylene Molecules

## II. Mean Amplitudes of Vibration and Related Quantities \*

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Calculated mean amplitudes of vibration for ethylene, ethylene-d<sub>4</sub> and ethylene-t<sub>4</sub> are reported. For light ethylene also the  $\Sigma$  matrix, the mean-square perpendicular amplitudes, and the mean cross products are given. The algebraic expressions for the squared mean amplitudes of vibration in terms of the matrix elements are included.

In a previous article<sup>1</sup> a set of harmonic force constants for ethylene molecules was proposed. The normal-coordinate transformation matrices  $L$  ( $S = LQ$ ) were also given for ethylene and ethylene-d<sub>4</sub>. In the present work further spectroscopic calculations have been performed for the mentioned molecules, using the reported force field.<sup>1</sup> The scope has been extended by including the tritium compound ethylene-t<sub>4</sub>. For the  $L$  matrix of this compound, see Table 1.

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*Mean-square amplitude matrix.* It may be of interest to investigate the influence of certain approximations on the vibrational mean-square amplitude matrix  $\Sigma$ .<sup>2</sup> The approximations in question are (a) separation of high and low frequencies, (b) assumption of a simplified molecular model. They have also been used in the previous work,<sup>1</sup> where the resulting force constants from the various approximations are reported. The present Table 2 for  $\Sigma$  at 298°K is equivalent to Table 5 of Ref.<sup>1</sup> for the force constant matrix. The approximate values are seen to deviate very little from those of the rigorous calculation, as could be expected. For the sake of completeness also the out-of-plane  $\Sigma$  matrix elements are given (Table 3).

The  $\Sigma$ -matrix elements have been calculated using the equation

$$\Sigma = L\tilde{A}L$$

\* Ref.<sup>1</sup> is regarded as Part I of this series. The project of both parts has been supported by *Norges tekniske høgskoles fond* (1963 and 1964).

Table 1. L matrix elements for ethylene- $t_4$  in (Amu) $^{-1/2}$ .

	1	2	3	1	2
$S_1(A_g)$	0.603866	0.107188	0.018135		
$S_2(A_g)$	-0.203387	0.348408	-0.062116		
$S_3(A_g)$	0.157518	-0.238321	0.690048		
$S_1(B_{1g})$				0.672025	0.038011
$S_2(B_{1g})$				-0.561504	1.017808
	1	2	1	2	
$S_1(B_{2u})$		0.673092	0.003083		
$S_2(B_{2u})$		-0.125023	0.669219		
$S_1(B_{3u})$				0.613359	-0.016238
$S_2(B_{3u})$				0.153187	0.730964
	( $B_{2g}$ )	( $A_u$ )	( $B_{1u}$ )		
$S$	1.430610	0.336955	1.065303		

Table 2. In-plane mean-square amplitude ( $\Sigma$ ) matrix for ethylene at 298°K ( $\text{Å}^2$  units).

$A_g$	$S_1$	<b>0.005116</b> (0.005102)*	<b>-0.000509</b> (0)	<b>0.000769</b> (0)
	$S_2$		<b>0.001830</b> (0.001784)	<b>-0.002312</b> (-0.002251)
	$S_3$		<b>0.001473**</b>	<b>0.017641</b> (0.017553)
$B_{1g}$	$S_1$	<b>0.006067</b> (0.006065)	<b>-0.002064</b> (0)	
	$S_2$		<b>0.028354</b> (0.027666)	
$B_{2u}$	$S_1$	<b>0.005727</b> (0.005727)	<b>-0.000458</b> (0)	
	$S_2$		<b>0.026925</b> (0.026889)	
$B_{3u}$	$S_1$	<b>0.005464</b> (0.005464)	<b>0.000496</b> (0)	
	$S_2$		<b>0.015500</b> (0.015456)	

\* In parentheses are given the values from approximate separation of high and low frequencies.

\*\* Approximate value based on the simplified model.

Table 3. Out-of-plane mean-square amplitude matrix elements for ethylene at 298°K (Å<sup>2</sup> units).

$B_{2g}$	0.063068
$A_u$	0.005672
$B_{1u}$	0.047281

where  $\Delta$  is a diagonal matrix with the elements

$$\Delta_i = (h/8\pi^2c\omega_i) \coth(hc\omega_i/2kT)$$

Here  $h$  is Planck's constant,  $c$  the velocity of light, and  $\omega_i$  represents the normal frequencies as wave numbers.  $k$  is Boltzmann's constant, and  $T$  the absolute temperature.

*Mean amplitudes of vibration.* The mean amplitudes of vibration ( $u$ )<sup>3</sup> at absolute zero and 298°K temperatures have been calculated for all the six types of distances in ethylene. The results are given in Table 4, along with some spectroscopic values calculated by Kuchitsu, and electron-diffraction results from Bartell and Bonham.<sup>4</sup>

Table 4. Mean amplitudes of vibration for ethylene (Å units).

Type	Spectroscopic Present		Kuchitsu*	Electron diffraction**
	$T = 0$	298°K		
Bonded C—H	0.07479	0.07479	0.0772	0.076 <sub>3</sub>
Nonbonded CH	0.09462	0.09498	0.0958	0.102 <sub>3</sub>
C=C	0.04273	0.04277	0.0419	0.043 <sub>3</sub>
(1,1)-HH	0.11817	0.11825		
<i>cis</i> -HH	0.16351	0.16534		
<i>trans</i> -HH	0.11458	0.11466		

\* Quoted by Bartell and Bonham; Ref.<sup>4</sup>

\*\* Ref.<sup>4</sup>

The squared values of  $u$  may be expressed as linear combinations of the  $\Sigma$ -matrix elements. These relations have been evaluated and are given in the following, where  $\Sigma$  is based on the symmetry coordinates previously defined.<sup>1</sup>  $R$  and  $D$  denote the equilibrium CH and CC distances, respectively, and  $2A$  is the equilibrium value of the HCH angle.

$$u^2(\text{Bonded C—H}) = \frac{1}{4}[\Sigma_1(A_g) + \Sigma_1(B_{1g}) + \Sigma_1(B_{2u}) + \Sigma_1(B_{3u})]$$

$$u^2(\text{Nonbonded CH}) = (R^2 + D^2 + 2RD\cos A)^{-1} \left\{ \frac{1}{4}(R + D\cos A)^2 [\Sigma_1(A_g) + \Sigma_1(B_{1g}) + \Sigma_1(B_{2u}) + \Sigma_1(B_{3u})] + (D + R\cos A)^2 \Sigma_2(A_g) + \frac{1}{4}RD[\Sigma_3(A_g) + \Sigma_2(B_{1g}) + \Sigma_2(B_{2u})] \right\}$$

$$\begin{aligned}
& + \Sigma_2(B_{3u})] \sin^2 A + (R + D \cos A) (D + R \cos A) \Sigma_{12}(A_g) + (RD)^{\frac{1}{2}} (D \\
& + R \cos A) \Sigma_{23}(A_g) \sin A \\
& + \frac{1}{2}(RD)^{\frac{1}{2}}(R + D \cos A)[\Sigma_{13}(A_g) + \Sigma_{12}(B_{1g}) + \Sigma_{12}(B_{2u}) + \Sigma_{12}(B_{3u})] \sin A \} \\
u^2(\text{C}=\text{C}) &= \Sigma_2(A_g) \\
u^2(1,1\text{-HH}) &= [\Sigma_1(A_g) + \Sigma_1(B_{3u})] \sin^2 A + (R/D)[\Sigma_3(A_g) + \Sigma_2(B_{3u})] \cos^2 A \\
& - (R/D)^{\frac{1}{2}}[\Sigma_{13}(A_g) + \Sigma_{12}(B_{3u})] \sin 2A \\
u^2(\text{cis-HH}) &= [\Sigma_1(A_g) + \Sigma_1(B_{2u})] \cos^2 A + \Sigma_2(A_g) + (R/D)[\Sigma_3(A_g) \\
& + \Sigma_2(B_{2u})] \sin^2 A \\
& + 2 \Sigma_{12}(A_g) \cos A + 2(R/D)^{\frac{1}{2}} \Sigma_{23}(A_g) \sin A + (R/D)^{\frac{1}{2}}[\Sigma_{13}(A_g) \\
& + \Sigma_{12}(B_{2u})] \sin 2A \\
u^2(\text{trans-HH}) &= (4R^2 + D^2 + 4RD \cos A)^{-1} \{ (2R + D \cos A)^2 [\Sigma_1(A_g) + \Sigma_1(B_{1g})] \\
& + (D + 2R \cos A)^2 \Sigma_2(A_g) + RD[\Sigma_3(A_g) + \Sigma_2(B_{1g})] \sin^2 A \\
& + 2(2R + D \cos A)(D + 2R \cos A) \Sigma_{12}(A_g) + 2(RD)^{\frac{1}{2}}(D + 2R \cos A) \Sigma_{23} \\
& (A_g) \sin A \\
& + 2(RD)^{\frac{1}{2}}(2R + D \cos A)[\Sigma_{13}(A_g) + \Sigma_{12}(B_{1g})] \sin A \}
\end{aligned}$$

Some comments should be made on the C=C mean amplitude of vibration obtained by the consideration of the simplified model,<sup>1</sup> *viz.* a two-particle structure  $\text{CH}_2\text{CH}_2$ , vibrating as a diatomic molecule with the  $\omega_2$  frequency of ethylene. The result was 0.0384 Å, and deviates about  $-0.004$  Å or  $-10\%$  from the rigorous value in Table 4. We feel that this kind of approximation may be of practical importance, taking into account the minimum of labour required in many cases. In the present case the approximate C=C mean amplitude ( $u_0$ ) is simply obtained from

$$u_0^2 = 2\mu_{\text{H}}\mu_{\text{C}}(\mu_{\text{H}} + 2\mu_{\text{C}})^{-1}A_2$$

where  $\mu_{\text{H}}$  and  $\mu_{\text{C}}$  denote the inverse masses of the H and C atoms, respectively.

Table 5. Mean-square perpendicular amplitudes for ethylene at 298°K (Å<sup>2</sup> units).

Type	in-plane	out-of-plane
Bonded C—H	0.014892	0.014135
Nonbonded CH	0.009905	0.010662
C=C	0.000920	0.001076
(1,1)-HH	0.026170	0.016558
<i>cis</i> -HH	0.011201	0.027767
<i>trans</i> -HH	0.017274	0.011210

Table 6. Mean cross products for ethylene at 298°K (Å<sup>2</sup> units).

Type	in-plane mean cross product
Bonded C—H	0.000047
Nonbonded CH	0.003826
<i>trans</i> -HH	0.004771

Table 7. Mean amplitudes of vibration for ethylene-d<sub>4</sub> and ethylene-t<sub>4</sub> (Å units).

Type	C <sub>2</sub> D <sub>4</sub>		C <sub>2</sub> T <sub>4</sub>	
	T = 0	298°K	T = 0	298°K
Bonded C—H	0.06410	0.06410	0.05892	0.05892
Nonbonded CH	0.08148	0.08250	0.07502	0.07666
C=C	0.04263	0.04268	0.04255	0.04262
(1,1)-HH	0.09965	0.10002	0.09024	0.09103
<i>cis</i> -HH	0.13781	0.14297	0.12478	0.13298
<i>trans</i> -HH	0.09679	0.09709	0.08776	0.08834

*Mean-square perpendicular amplitudes, and mean cross products.* The generalized mean-square amplitudes<sup>5</sup> may all be expressed as linear combinations of the  $\Sigma$  matrix elements. As for the mean-square perpendicular amplitudes and mean cross products the algebraic expressions are too complex to be reproduced here. We only give some numerical results for ethylene at  $T = 0$  and 298°K. The in-plane and out-of-plane perpendicular amplitudes, here referred to as  $\langle \Delta x^2 \rangle$  and  $\langle \Delta y^2 \rangle$ , respectively (Table 5), are seen to be of the same order of magnitude for corresponding atom pairs. Somewhat surprisingly even some of the  $\langle \Delta x^2 \rangle$  are significantly greater than the corresponding  $\langle \Delta y^2 \rangle$ . This is true for the (1,1)-HH and *trans*-HH atom pairs.

Most of the mean cross products vanish because of symmetry. Only three in-plane quantities of  $\langle \Delta z \Delta x \rangle$  remain, and are given in Table 6 for ethylene at  $T = 0$  and 298°K.

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All the above mentioned quantities have also been computed for ethylene-d<sub>4</sub> and ethylene-t<sub>4</sub>. Only the mean amplitudes of vibration are reported here (Table 7), as these results are supposed to be those of the greatest interest.

#### REFERENCES

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