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Force constants for the ethylene molecule developed from Green's function technique[a]

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There have been numerous determinations of the force constants (FC's) for the ethylene molecule,[1-3] using different models or different sets of constraint equations. In this paper, we have calculated the FC matrix for ethylene in Cartesian coordinates (F_x) using the Green's function technique (GFT) developed by Wolfram and Asgharian.[4] According to the GFT, a unique set of FC's is determined from isotopic frequency data without imposing any *a priori* constraints on the force field. The only FC's which are zero are those which vanish because of symmetry considerations. All others are determined uniquely by six mixing parameters. This is in contrast to many reported FC calculations which utilize less fundamental constraint relations to reduce the number of FC's. The experimental geometry, mixing parameters, notation, and vibrational frequencies used in this paper are taken from Ref. 4. However, mixing parameter C_5 was misprinted as 0.523; the correct value is 0.532.[5]

The Cartesian FC's (F_{jk}) are calculated using $F_{jk} = \sum_l \lambda_l = U_{jl} U_{kl}^* (M_j M_k)^{1/2}$, where the matrix elements U_{jl} are given in Ref. 4 and M_j is the mass of the jth atom. The coordinate system used is shown in Fig. 1 of Ref. 4. The in plane (IP) and out of plane (OP) FC matrices for ethylene are given in Tables I and II, respectively. There is no coupling between the IP and OP modes. (As a consistency check, we verified that diagonaliza-

TABLE I. In-plane force constants of ethylene in Cartesian coordinates.[a,b]

	C_{1_x}	C_{1_y}	C_{2_x}	C_{2_y}	H_{3_x}	H_{3_y}	H_{4_x}	H_{4_y}	H_{5_x}	H_{5_y}	H_{6_x}	H_{6_y}
C_{1_x}	12.896	0.0	−8.486	0.0	−0.177	−0.036	−2.028	1.934	−0.177	0.036	−2.028	−1.934
C_{1_y}	0.0	9.739	0.0	−0.782	1.110	−4.281	0.891	−0.197	−1.110	−4.281	−0.891	−0.197
C_{2_x}	−8.486	0.0	12.896	0.0	−2.028	1.934	−0.177	−0.036	−2.028	−1.934	−0.177	0.036
C_{2_y}	0.0	−0.782	0.0	9.739	0.891	−0.197	1.110	−4.281	−0.891	−0.197	−1.110	−4.281
H_{3_x}	−0.177	1.110	−2.028	0.891	1.788	−1.874	0.012	−0.076	0.531	0.054	−0.126	−0.105
H_{3_y}	−0.036	−4.281	1.934	−0.197	−1.874	4.647	−0.076	−0.132	−0.054	0.150	0.105	−0.187
H_{4_x}	−2.028	0.891	−0.177	1.110	0.012	−0.076	1.788	−1.874	−0.126	−0.105	0.531	0.054
H_{4_y}	1.934	−0.197	−0.036	−4.281	−0.076	−0.132	−1.874	4.647	0.105	−0.187	−0.054	0.150
H_{5_x}	−0.177	−1.110	−2.028	−0.891	0.531	−0.054	−0.126	0.105	1.788	1.874	0.012	0.076
H_{5_y}	0.036	−4.281	−1.934	−0.197	0.054	0.150	−0.105	−0.187	1.874	4.647	0.076	−0.132
H_{6_x}	−2.028	−0.891	−0.177	−1.110	−0.126	0.105	0.531	−0.054	0.012	0.076	1.788	1.874
H_{6_y}	−1.934	−0.197	0.036	−4.281	−0.105	−0.187	0.054	0.150	0.076	−0.132	1.874	4.647

[a] All force constants are in mdyn/Å.
[b] Coordinates are defined in Ref. 4.

TABLE II. Out-of-plane force constants of ethylene in Cartesian coordinates.[a,b]

	C_{1_z}	C_{2_z}	H_{3_z}	H_{4_z}	H_{5_z}	H_{6_z}
C_{1_z}	1.658	−0.707	−0.560	0.084	−0.560	0.084
C_{2_z}	−0.707	1.658	0.084	−0.560	0.084	−0.560
H_{3_z}	−0.560	0.084	0.368	0.193	0.045	−0.131
H_{4_z}	0.084	−0.560	0.193	0.368	−0.131	0.045
H_{5_z}	−0.560	0.084	0.045	−0.131	0.368	0.193
H_{6_z}	0.084	−0.560	−0.131	0.045	0.193	0.368

[a] All force constants are in mdyn/Å.
[b] Coordinates are defined in Ref. 4.

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TABLE III. Force constants of ethylene in internal coordinates.[a]

	q_1	q_2	q_3	q_4	q_5	q_6	q_7	q_8	q_9	q_{10}	q_{11}	q_{12}
q_1	16.825	2.787	2.787	2.787	2.787	0.890	0.890	0.890	0.890	0.0	0.0	0.0
q_2	2.787	5.313	0.308	−0.202	0.218	−0.106	−0.112	0.208	0.038	0.0	0.0	0.0
q_3	2.787	0.308	5.313	0.218	−0.202	0.038	0.208	−0.112	−0.106	0.0	0.0	0.0
q_4	2.787	−0.202	0.218	5.313	0.308	0.208	0.038	−0.106	−0.112	0.0	0.0	0.0
q_5	2.787	0.218	−0.202	0.308	5.313	−0.112	−0.106	0.038	0.208	0.0	0.0	0.0
q_6	0.890	−0.106	0.038	0.208	−0.112	1.018	−0.026	0.077	0.388	0.0	0.0	0.0
q_7	0.890	−0.112	0.208	0.038	−0.106	−0.026	1.018	0.388	0.077	0.0.	0.0	0.0
q_8	0.890	0.208	−0.112	−0.106	0.038	0.077	0.388	1.018	−0.026	0.0	0.0	0.0
q_9	0.890	0.038	−0.106	−0.112	0.208	0.388	0.077	−0.026	1.018	0.0	0.0	0.0
q_{10}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.259	0.039	0.0
q_{11}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.039	0.259	0.0
q_{12}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.559

[a]In units of mdyn/Å, mdyn/rad, and mdyn Å/rad^2 for stretching–stretching, stretching–bending, and bending–bending FC's, respectively.

tion of the FC matrix yields the input vibrational frequencies exactly.)

In order to compare F_x with the internal FC's of other authors, we chose the following internal coordinates q_i: $q_1 = $ C–C stretch, $q_2 = C_1$–H_3 stretch, $q_3 = C_1$–H_5 stretch, $q_4 = C_2$–H_4 stretch, $q_5 = C_2$–H_6 stretch, $q_6 = \alpha_{312}$ $H_3C_1C_2$ bend, $q_7 = \alpha_{126}$ $C_1C_2H_6$ bend, $q_8 = \alpha_{421}$ $H_4C_2C_1$ bend, $q_9 = \alpha_{215}$ $C_2C_1H_5$ bend, $q_{10} = \theta_{2153}$ out-of-plane wag of atom C_2, $q_{11} = \theta_{1264}$ out of plane wag of atom C_1, $q_{12} = \tau$ torsion about C_1–C_2 axis. These coordinates are defined in the manner specified in QCPE program #342,[6] which was used to develop the appropriate B matrix. Since the B matrix is not square, it was inverted using the technique described by Pulay,[7] Next, the FC matrix in internal coordinates (F_{int}) was calculated using: $F_{int} = (B^\dagger)^{-1} F_x B^{-1}$. The results are given in Table III.

These FC's are calculated with the experimental frequencies used by Duncan et al.[2] and the mixing parameters of Ref. 4. We obtained values of 16.825, 5.313, and 2.787 mdyn/Å for the CC stretch, CH stretch, and CC stretch CH stretch interaction FC's, respectively. The corresponding values obtained by Duncan et al. are 9.395, 5.598, and 0.182. While the CH stretch FC's are in reasonable agreement, the CC stretch and CC stretch CH stretch interaction FC's obtained from the GFT are nearly 2 and 15 times the respective FC's obtained by Duncan et al. The source of these discrepancies is not clear; however, it may be an effect of the

constraint equations used in conventional FC calculations. An interesting comparison can be made between our torsional FC and that of Duncan et al. We obtained 0.559 mdyn Å/rad^2 while they obtained 0.760 (after removing the CH bond length scaling factor). The torsional FC is completely determined by group theory and its value depends solely on the input vibrational frequency. Since we used the same frequencies as Duncan et al., it is difficult to resolve this discrepancy.

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