Normal Coordinates and Force Constants of

Ethylene Molecules

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Normal frequencies for ethylene and ethylene-d_4 were derived from observed fundamentals (taken from literature) by a systematic use of Dennison's anharmonicity correction. The sets of normal frequencies were made to fit not only the familiar product rule for isotopic molecules, but also (a) the separated product rule from separation of high and low frequencies, and (b) a product rule obtained from the consideration of a simplified molecular model.

A set of force constants, which reproduce the derived normal frequencies, was established. The corresponding L-matrices were evaluated numerically for ethylene and ethylene-d_4.

In the present work a new set of harmonic force constants for ethylene molecules is presented. It is based on a set of normal frequencies, which satisfy certain special requirements. The complete L-matrix for ethylene and ethylene-d_4 is presented, as far as we know for the first time. Previous spectroscopic work on ethylene molecules is reviewed briefly.

FUNDAMENTAL FREQUENCIES

Herzberg's assignment of frequencies for ethylene molecules, published in 1945 [1] contained several dubious points. New measurements and assignments were published in 1950 by Rank, Shull and Axford [2] (C_2H_4), and Arnett and Crawford [3] (C_2H_4 and C_2D_4). The assignment has been discussed by Torkington.[4] Plyler [5] has suggested to replace the value of $\nu_5 = 3273.3$ cm^{-1} for C_2H_4 by 3075 cm^{-1}, obtained from studies of combination bands. The same value is also suggested by Torkington [6] in his modification of Herzberg's assignment.[1] This frequency may be observed as a Raman line in liquid ethylene. The next pioneer work to be mentioned is due to Crawford, Lancaster and Inskeep,[7] who calculated force constants for ethylene. These investigators also prefer the value of 3075 cm^{-1} for ν_5. Apart from this value they adher to the assignment from Refs.[2,3] In addition, ν_{10} for C_2D_4 from Charette and de

Hemptinne [8] is adopted. The same assignment has also been adopted by Golike, Mills, Person and Crawford,[9] and a recent work of Scherer and Overend.[10] The latter investigators calculated Urey-Bradley force constants. Stoicheff [11] has given an elegant solution of the question of the ν_5 frequency, for which he found (3108 ± 5) cm^{-1}. In a later work by Shimanouchi [12] the assignment of Arnett and Crawford [3] was used apart from the frequency of ν_5, for which Stoicheff's value [11] was adopted. More recent and accurate measurements of Feldman, Romanko and Welsh [13] include the value of $\nu_5 = 3102.5$ cm^{-1}. Brodersen [14] has collected data of fundamental frequencies from various sources. His set has later been revised [15] according to the results of Feldman, Romanko and Welsh.[13] The revised set has recently been adopted in a work of Lehmann.[16] Some of the measurements on C_2H_4 in the infrared have been verified by Brecher and Halford [17] in connection with their recent investigation on crystalline ethylene. In this connection also the still more recent work of Dows [18,19] should be mentioned.

In Table 1 the presently adopted fundamental frequencies for ethylene and ethylene-d_4 are given, along with some of the previous suggestions. Gas frequencies were preferred when available.

Table 1. Assignments for ethylene and ethylene-d_4.

	Species,	No.	a	b	c *	Present *
	A_g	1	3019.3	3019.3	3026	3026.4
		2	1623.3	1623.3	1623	1622.6
		3	1342.4	1342.4	1342	1342.2
	A_u	4	825	1027	1027	1027
	B_{1g}	5	3272.3	3272.3	3103	3102.5
C_2H_4		6	1050	1236	1236	1236
	B_{1u}	7	949.2	949.2	949	949.2
	B_{2g}	8	943	943	947	947
	B_{2u}	9	3105.5	3105.5	3106	3105.5
		10	995	810.3	810	810.3
	B_{3u}	11	2989.5	2989.5	2990	2989.5
		12	1443.5	1443.5	1444	1443.5
	A_g	1	2251	2251	2260	2260
		2	1515	1515	1518	1518
		3	981	981	985	985
	A_u	4		726	726	726
	B_{1g}	5	2304	2304	2310	2310
C_2D_4		6	883	1009	1011	1011
	B_{1u}	7	720.0	720.0	720	720
	B_{2g}	8	780	780	785	785
	B_{2u}	9	2345	2345	2345	2345
		10			584	
	B_{3u}	11	2200.2	2200.2	2200	2200.2
		12	1077.9	1077.9	1078	1077.9

[a] From Herzberg [1].
[b] From Arnett and Crawford [3]; for C_2H_4 also Rank, Shull and Axford.[2]
[c] From Brodersen and Langseth [15].
* Collected from literature.

STRUCTURAL PARAMETERS

The frequently cited data of Gallaway and Barker [20] have been replaced by more recent measurements from electron diffraction,[21,22] and spectroscopic methods in infrared [23] and Raman.[24] The results are quoted in Table 2. It

Table 2. Structural parameters for ethylene.

C=C (Å)	C−H (Å)	∠ HCH	Method
1.330 ± 0.003	1.074 ± 0.005	116°	Electr.diff.[21]
1.333 ± 0.002	1.084 ± 0.003	115.5 ± 0.6°	Electr.diff.[22]
1.337 ± 0.003	1.086 ± 0.003	117°22′ ± 1°	Infrared [23]
1.339 ± 0.002	1.086 ± 0.003	117°34′ ± 30′	Raman [24]

should be pointed out that none of the mentioned methods give directly the *equilibrium* parameters, but the small deviations are not substantial for our purpose. We have adopted

$$CH = CD = 1.086 \text{ Å}$$
$$CC = 1.337 \text{ Å}$$
$$\angle HCH = \angle DCD = 117°22′$$

for ethylene and ethylene-d_4.

NORMAL FREQUENCIES

Some principles for systematization of Dennison's method for anharmonicity corrections

A systematic procedure of anharmonicity corrections for ethylene and ethylene-d_4 was evaluated by combining Dennison's method [25] with certain additional approximations.

Dennison's method. According to Dennison [25] the anharmonicity constants (x) are defined by

$$\nu_i = (1 - x_i)\omega_i, \qquad \nu_i^* = (1 - x_i^*)\omega_i^*$$

where the normal frequencies (ω) are presumably required to fulfil the isotope rule (Teller-Redlich product rule).[26-29] In addition, the following assumption is made

$$x_i/x_i^* = \nu_i/\nu_i^*$$

The method is somewhat arbitrary, but has been adopted by many investigators (see, *e.g.*, Refs.[30-33]). Dennison's method allows an unambiguous computation of the anharmonicity constants for a symmetry species which contains only one frequency for each of the isotopic molecules. Another important case is that of a species with one high and one low frequency, when the separated isotope rule is utilized. The A_2'' frequencies of cyclopropane represent an

example of the latter case, for which the Dennison method has been applied.[33],[32] In ethylene there are no less than three species (B_{1g}, B_{2u}, B_{3u}) which may be treated in the way mentioned above.

In the above discussed cases only one frequency for each of the isotopic molecules is involved, when applying the Dennison method. For such cases, which are of special interest because of the unambiguity, some useful formulae will be given. Let the experimental and theoretical ratios be denoted by e and t, respectively, viz.

$$e = \nu/\nu^*, \qquad t = \omega/\omega^* = G^{1/2}(G^*)^{-1/2}$$

The expressions deduced for the anharmonic constants follow.

$$x = (t - e)/(t - 1), \qquad x^* = (t - e)/e(t - 1)$$

Separation of high and low frequencies. The approximate separation of high and low frequencies [34],[35],[28] is a well known and widely used method. It has proved to be of special importance for cases of molecules with (high) CH stretching frequencies, along with the corresponding deuterated compounds. When the separation of frequencies for two isotopic molecules is carried out, the isotope rule splits into separate isotope rules for the high and low frequencies, respectively. In this connection one interesting theorem should be noted: When the (approximate) separated isotope rules are fulfilled, also the validity of the conventional ("rigorous") isotope rule is guaranteed.[36] As already mentioned, the separated isotope rules are very useful in connection with the Dennison anharmonicity corrections.

Consideration of simplified models. In many cases a useful approximation may be obtained by considering a simplified molecular model, based on the skeleton structure of the molecule (see, *e.g.*, Refs. [37-41]). By this method a new type of approximate isotope rules, which contain the skeleton frequencies only, may be obtained.

Application to ethylene and ethylene-d_4

Classification of normal modes. The symmetry species and the corresponding normal vibrations of ethylenes may be classified in the following systematic way.

(a) The totally symmetric species A_g. This species contains 3 in-plane modes, including the totally symmetric CH (or CD) stretching, and the CC stretching.

(b) The non-totally symmetric species for inplane vibrations (B_{1g}, B_{2g}, B_{3g}). Each of these species contains two normal modes, one of them being that of a CH (CD) stretching.

(c) The symmetry species for out-of-plane vibrations (B_{2g}, A_u, B_{1u}), containing one normal mode each.

Simplified model. The simplified molecular model for ethylene here considered, is simply the two-particle structure $CH_2 \cdot CH_2$. This system is assumed, as an approximation, to vibrate with the normal frequency of CC stretching in ethylene (ω_2). The problem may be treated as a diatomic molecule, and the following expression is derived for the appropriate force constant.

$$\lambda = GF = 2\mu_H\mu_C(\mu_H + 2\mu_C)^{-1} F$$

Here μ_H and μ_C denote the inverse masses of the H and C atoms, respectively, and $\lambda = 4\pi^2 c^2 \omega_2{}^2$ (ω_2 in cm^{-1}). If the same model is adapted to the deuterated compound, $viz.$ $CD_2 \cdot CD_2$, the following isotope rule may be derived.

$$\lambda/\lambda^* = \omega_2{}^2/(\omega_2{}^*)^2 = \mu_H(\mu_H + 2\mu_C)^{-1}\mu_D{}^{-1}(\mu_D + 2\mu_C) \qquad (1)$$

Here the asterisk is used, as usual, to identify the deuterated compound, and μ_D is adopted instead of $\mu_H{}^*$.

Species A_g. In ethylene ω_1 represents the frequency of totally symmetric CH stretching. In our notation $w_1{}^*$ is used to identify the corresponding frequency in ethylene-d_4. After separation of the high frequencies in ethylene and ethylene-d_4 (ω_1 and $\omega_1{}^*$, respectively) from the remaining frequencies of A_g (ω_2, ω_3 and $\omega_2{}^*$, $\omega_3{}^*$, respectively), the following separated isotope rules are obtained.

$$\omega_1{}^2/(\omega_1{}^*)^2 = (\mu_H + 2\mu_C\cos^2A)(\mu_D + 2\mu_C\cos^2A)^{-1} \qquad (2)$$
$$\omega_2{}^2\omega_3{}^2/(\omega_2{}^*)^2(\omega_3{}^*)^2$$
$$= \mu_H{}^2(\mu_H + 2\mu_C\cos^2A)^{-1}\mu_D{}^{-2}(\mu_D + 2\mu_C\cos^2A)$$

Here A denotes one half of the equilibrium HCH (or DCD) angle. If the validity of the approximation of eqn. (1) is maintained, a separate isotope rule for ω_3 and $\omega_3{}^*$ may be derived as follows.

$$\omega_3{}^2/(\omega_3{}^*)^2 = \mu_H(\mu_H + 2\mu_C\cos^2A)^{-1}(\mu_H + 2\mu_C)\mu_D{}^{-1}(\mu_D + 2\mu_C\cos^2A)(\mu_D + 2\mu_C)^{-1} \quad (3)$$

The approximate eqns. (1) — (3) are exactly consistent with the over-all "rigorous" isotope rule:

$$\omega_1{}^2\omega_2{}^2\omega_3{}^2/(\omega_1{}^*)^2(\omega_2{}^*)^2(\omega_3{}^*)^2 = \mu_H{}^2\mu_D{}^{-2}$$

All the anharmonicity constants for species A_g may be determined without ambiguity by Dennison's method with the additional assumptions of eqns. (1)—(3).

The other species. From the given discussion it follows that all the remaining anharmonicity constants may be determined without ambiguity. They are obtained immediately in the case (c) of the given classification, and after separation of high and low frequencies in the case of (b).

Numerical computations. The anharmonicity constants and normal frequencies were computed according to the procedure outlined above. For the final results, see Table 4. In Table 3 the numerical values for the theoretical (t) and experimental (e) frequency ratios of the isotope rules are given.

We wish to point out the remarkably good agreement between t and e for the frequency No. 2. Here $t = 1.0694$ refers to the approximation of simplified model. The good agreement makes it justified to apply the described procedure for species A_g with confidence.

Table 3. Frequency ratios of the isotope rules: t(theoretic) $= \Pi(\omega/\omega^*) = |G|^{1/2}|G^*|^{-1/2}$, e(experimental) $= \Pi\,(\nu/\nu^*)$

Frequencies		Rigorous		Separated frequencies		Simplified model	
A_g	1			t:	1.38400		
				e:	1.33912		
	2	t:	1.99847			t:	1.06939
		e:	1.95047	t:	1.44398	e:	1.06891
	3			e:	1.45653		
A_u	4	t:	1.41367				
		e:	1.41460				
B_{1g}	5			t:	1.34238		
		t:	1.64744	e:	1.34307		
		e:	1.64198	t:	1.22725		
	6			e:	1.22255		
B_{1u}	7	t:	1.32194				
		e:	1.31833				
B_{2g}	8	t:	1.21085				
		e:	1.20637				
B_{2u}	9			t:	1.34238		
		t:	1.86879	e:	1.32431		
		e:	1.83325	t:	1.39215		
	10			e:	1.38431		
B_{3u}	11			t:	1.38400		
		t:	1.86879	e:	1.35874		
		e:	1.81960	t:	1.35029		
	12			e:	1.33918		

Some of the anharmonicity constants came out with negative figures. This situation contradicts usual experience. It seems not possible, however, to remove this feature by reasonable means without changing the fundamental frequencies. Therefore the negative values had to be accepted for the time being.

In species B_{2u} the value of $x_2 = 0.02$ was assumed because of the lack of an experimental value for ν_{10}.* With this assumption the value of $\nu_{10}^* = 585.35$ cm^{-1} was calculated and was found in very good agreement with calculated values of Arnett and Crawford [3] (586 cm^{-1}) and Crawford, Lancaster and Inskeep [7] (589 cm^{-1}).*

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* When the calculations were performed we were not aware of the experimental value of 584 cm^{-1}, reported by Charette and de Hemptinne.[8] The discrepancy is so small that it was not found worth while performing a recalculation.

Table 4. Fundamental frequencies (ν), anharmonicity constants (x) and normal frequencies (ω).

C_2H_4		$\nu(cm^{-1})$	x	$\omega(cm^{-1})$
A_g	1	3026.4	0.116879	3426.93
	2	1622.6	0.006932	1633.93
	3	1342.2	−0.035260	1296.49
A_u	4	1027	−0.002246	1024.70
B_{1g}	5	3102.5	−0.002027	3096.23
	6	1236	0.020686	1262.11
B_{1u}	7	949.2	0.011213	959.96
B_{2g}	8	947	0.021257	967.57
B_{2u}	9	3105.5	0.052786	3278.56
	10	810.3	0.02(*ass.*)	826.84
B_{3u}	11	2989.5	0.065772	3199.96
	12	1443.5	0.031714	1490.78

C_2D_4		$\nu(cm^{-1})$	x	$\omega(cm^{-1})$
A_g	1	2260	0.087281	2476.11
	2	1518	0.006485	1527.91
	3	985	−0.025876	960.16
A_u	4	726	−0.001588	724.85
B_{1g}	5	2310	−0.001509	2306.52
	6	1011	0.016921	1028.40
B_{1u}	7	720	0.008506	726.17
B_{2g}	8	785	0.017620	799.08˙
B_{2u}	9	2345	0.039860	2442.35
	10	585.35	0.014448	593.93
B_{3u}	11	2200.2	0.048406	2312.12
	12	1077.9	0.023682	1104.04

The present anharmonic corrections are different from those of Arnett and Crawford,[3] who corrected only the CH and CD stretching frequencies. They are also different from the "adjustment of experimental material" of Brodersen.[14] The present normal frequencies are exactly consistent with the isotope rule requirements, not only for the conventional model, but also for the (*a*) model with separated frequencies, and (*b*) the simplified two-particle model. This properties make the normal frequencies very well suitable for comparative studies of the various approximate treatments.

SYMMETRY COORDINATES

The force-constant calculations, which are going to be reported, are based on a set of symmetry coordinates, specified in the following:

$$S_1(A_g) = (1/2)(r_1 + r_2 + r_3 + r_4)$$
$$S_2(A_g) = d$$
$$S_3(A_g) = (1/2)(RD)^{1/2}(\beta_1 + \beta_2 + \beta_3 + \beta_4)$$
$$S_1(B_{1g}) = (1/2)(r_1 - r_2 + r_3 - r_4)$$
$$S_2(B_{1g}) = (1/2)(RD)^{1/2}(\beta_1 - \beta_2 + \beta_3 - \beta_4)$$
$$S_1(B_{2u}) = (1/2)(r_1 - r_2 - r_3 + r_4)$$

$$S_2(B_{2u}) = (1/2)(RD)^{1/2}[\beta_1 - \beta_2 - \beta_3 + \beta_4)$$
$$S_1(B_{3u}) = (1/2)(r_1 + r_2 - r_3 - r_4)$$
$$S_2(B_{3u}) = (1/2)(RD)^{1/2}(\beta_1 + \beta_2 - \beta_3 - \beta_4)$$
$$S(B_{2g}) = 2^{-1/2}(RD^{1/2})(\gamma_1 - \gamma_2)$$
$$S(A_u) = R\ \varphi$$
$$S(B_{1u}) = 2^{-1/2}(RD)^{1/2}(\gamma_1 + \gamma_2)$$

This is a complete set of symmetry coordinates (without redundants) for the ethylene molecular model of symmetry D_{2h}. Angle deformations have been multiplied by the constant $(RD)^{1/2}$ or R. Here R and D denote the equilibrium bond lengths of CH(CD) and CC, respectively. The notation used for the various types of displacements is as follows.

r:CH (CD) stretching.
d:CC stretching.
β:in-plane HCC (DCC) bending.
γ:out-of-plane bending.
φ:torsion.

The subscripts of r and β are consistent with the numbering of hydrogen atoms from 1 to 4 with 1 and 2 bonded to the same C atom, and $1-3$ in *trans* position. γ_1 includes the motion of the atoms 1 and 2, and γ_2 that of 3 and 4.

Different sets of symmetry coordinates for ethylene type molecules have been proposed. Our symmetry coordinates appear to be proportional to those of Arnett and Crawford,[3] in spite of the fact that our choise of in-plane valence angle bendings is essentially different. Morino et al.[42] in their study of C_2F_4 used another set of symmetry coordinates, based on valence coordinates containing redundancies, which later on were removed. This set has been adopted by Mann et al.[43] Hisatsune investigated N_2O_4,[44,45] which also is an ethylene type molecule. Hereby he utilized the coordinate sets of both Arnett and Crawford [3] and Morino et al.[42] For further references to theoretical studies on ethylene type molecules, see Refs. [12,14,46] Earlier work is summarized in the mentioned paper of Morino et al.[42]

FORCE CONSTANTS

Species A_g. Only five equations (2 linear, 2 quadratic and 1 cubic) are available for the six desired force constants, when using the secular equations for normal frequencies of the isotopic molecules here considered. To find a reasonable additional assumption, we considered the G-matrix in terms of the valence coordinates. For the two matrix elements corresponding to the coordinate pairs of $r_4(RD)^{1/2} \beta_1$ and $r_4(RD)^{1/2} \beta_2$, respectively, one finds [47,48]

$$g(r_4\beta_1) = (R/D)^{1/2}\mu_C \sin A$$
$$g(r_4\beta_2) = -g(r_4\beta_1) = -(R/D)^{1/2}\mu_C \sin A$$

This relation supports the following approximation introduced for the corresponding interaction force constants:

$$f(r_4\beta_2) = -f(r_4\beta_1)$$

Only this additional assumption was made, and the equations were solved for the force constants with the result given in Table 5 (in boldface figures). During

Table 5. In-plane force constants of the symmetrized F matrix (mdyne/Å units).

A_g	S_1	6.78460	1.00232	−0.11082
		(6.66989) *	(0)	(0)
			10.75973	1.51281
	S_2		(10.73559)	(1.52564)
			11.02183 **	
				0.96302
	S_3			(0.96170)
B_{1g}	S_1	5.14516	0.19481	
		(5.07022)	(0)	
			0.45585	
	S_2		(0.45510)	
B_{2u}	S_1	5.68803	0.03269	
		(5.68495)	(0)	
			0.31691	
	S_2		(0.31689)	
B_{3u}	S_1	5.82683	−0.11082	
		(5.81563)	(0)	
			0.95955	
	S_2		(0.95929)	

* In parentheses are given the force constants from the approximate separation of high and low frequencies.
** Approximate force constant based on the simplified model.

the computation it was easy to select one preferable set from the different solutions of quadratic equations. The results from approximate calculations (after separation of high and low frequencies, and using the simplified model) were very useful as a guide for the destination of accepted solutions.

The other species. The remaining force constants were calculated from the appropriate secular equations without further assumptions. The results are collected in Table 5 (in-plane force constants) and Table 6 (out-of-plane force constants).

Table 6. Out-of-plane force constants (mdyne/Å units).

B_{2g}	0.15524
A_u	1.81997
B_{1u}	0.20559

Approximate force constants. The normal frequencies for both of the isotopic ethylenes here considered are reproduced accurately by the computed set of force constants. Moreover, the normal frequencies have been derived in such a manner to be reproduced also by the approximate force constants

obtained by separation of high and low frequencies. Finally, ω_2 and ω_2* (*i.e.* the CC stretching frequencies in C_2H_4 and C_2D_4, respectively) are also reproduced by the force constant obtained from the consideration of the simplified two-particle model. The approximate force constants are included in Table 5.

Force constants in the notation of earlier work. It was desired to compare the presently evaluated force constants from the rigorous calculations (Table 5; boldface figures, and Table 6) with the frequently quoted force constants from Arnett and Crawford [3] (out-of-plane), and Crawford, Lancaster and Inskeep [7] (in-plane). Therefore we transformed our force constants to those of the notation from the mentioned pioneer works. The result follows.

			Present	Crawford, Lancaster and Inskeep	Arnett and Crawford
Species A_g:	K_1	=	6.78460	(6.1988)	
	k_2^1	=	0.50116	(−0.0039)	
	k_1	=	0.06148	(0.3401)	
	k_6^1	=	−0.83928	(−0.8467)	
	K_0	=	10.75973	(10.8956)	
	A_1	=	0.59280	(0.6518)	
Species A_u:	$\varDelta$	=	0.62341		(0.6260)
Species B_{1g}:	K_2	=	5.1452	(6.1529)	
	k_3	=	0.21615	(0.5057)	
	B_1	=	1.12241	(1.1403)	
Species B_{1u}:	H_1	=	0.93689		(0.9190)
Species B_{2g}:	H_2	=	0.70745		(0.6846)
Species B_{2u}:	K_3	=	5.68803	(6.0137)	
	k_4	=	0.03627	(1.3685)	
	B_2	=	0.78031	(1.3894)	
Species B_{3u}:	K_4	=	5.82683	(6.1394)	
	k_2	=	0.06148	(0.3401)	
	A_2	=	0.59066	(0.5886)	

The differences between our force constants and those from the mentioned previous work may seem surprisingly large in general. Probably they may be attributed mainly to differences in normal frequencies. As for the principal force constant for the CC stretching, there is a very good agreement, *viz.* our value of 10.75973 *vs.* 10.8956 from Crawford, Lancaster and Inskeep. The principal force constant for CH (CD) stretching is 5.86115 from our calculations *vs.* 6.1262 from Crawford, Lancaster and Inskeep.

L-MATRICES

Golike, Mills, Person and Crawford [9] have given numerical values for L^{-1}-matrix elements of some species for ethylene molecules. In the present work the complete L-matrices (rather than L^{-1}) were evaluated for ethylene and ethylene-d_4, using the standard method of characteristic vectors of the GF matrix.[35,28] The numerical results are given in Table 7 (ethylene) and Table 8 (ethylene-d_4).

Table 7. L matrix elements for ethylene in $(Amu)^{-\frac{1}{2}}$

	1	2	3	1	2
$S_1(A_g)$	1.017488	−0.004974	0.040511		
$S_2(A_g)$	−0.074510	0.331987	−0.225492		
$S_3(A_g)$	0.037129	0.300810	1.130945		
$S_1(B_{1g})$				1.055070	−0.019080
$S_2(B_{1g})$				−0.294913	1.441309

	1	2	1	2
$S_1(B_{2u})$	1.055241	−0.001975		
$S_2(B_{2u})$	−0.075682	1.127334		
$S_1(B_{3u})$			1.018267	0.008943
$S_2(B_{3u})$			0.070352	1.168739

	(B_{2g})	(A_u)	(B_{1u})
S	1.884555	0.582904	1.624738

Table 8. L matrix elements for ethylene-d_4 in $(Amu)^{-\frac{1}{2}}$

	1	2	3	1	2
$S_1(A_g)$	0.734529	0.035790	0.023386		
$S_2(A_g)$	−0.133291	0.375093	−0.090284		
$S_3(A_g)$	0.093753	−0.183740	0.847480		
$S_1(B_{1g})$				0.785938	0.015845
$S_2(B_{1g})$				−0.454297	1.160962

	1	2	1	2
$S_1(B_{2u})$	0.786096	0.001424		
$S_2(B_{2u})$	−0.105893	0.809487		
$S_1(B_{3u})$			0.735746	−0.006682
$S_2(B_{3u})$			0.119420	0.864009

	(B_{2g})	(A_u)	(B_{1u})
S	1.556388	0.412333	1.229052

Note: All the reported decimals in Tables 3—8 are not necessarily significant, but have been included to preserve mathematical consistency.

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