Relationship Between the Zero Point Energy of a Polyatomic Molecule and its Molecular Structure*

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Criteria are established for the definition of the mean characteristic eigenvalue, λ_0, of a system of coupled harmonic oscillators. The first criterion is that λ_0 lead to a convergent series for the zero point energy of the systems; the second criterion is that λ_0 be obtained directly from the matrix elements of the equations of motion, without solution for the individual eigenvalues. Two general types of λ_0's are found and their properties are discussed. Detailed application is made to the zero point energy differences of the isotopic methanes, ethylenes and benzenes.

Introduction

If it is possible to define a mean characteristic eigenvalue, λ_0, for the molecular vibrations of a polyatomic molecule such that

$$0 < \lambda_k/\lambda_0 < 2$$

for all eigenvalues λ_k of the molecule, then it is possible to express the total zero point energy of the molecule in terms of the moments of the eigenvalues and the characteristic eigenvalue λ_0. This theorem follows directly from the Taylor series expansion for the zero point energy

$$\varepsilon_0 = \tfrac{1}{2}\hbar\,\omega_0 \sum_{k}^{3n-6} \left[1 + \sum_{p=1}^{\infty} \frac{(-1)^{p+1}(2p-2)!}{2^{2p-1}(p-1)!(p)!}\,(X_k-1)^p\right], \quad [|X_k-1| \leqq 1] \tag{1}$$

given by BIGELEISEN and GOLDSTEIN [1]. In equation (1) the defined quantities are:

$$X_k = \lambda_k/\lambda_0,\ \lambda_k = \omega^2{}_k = 4\pi^2\nu^2{}_k\,,$$

and ε_0 is the total zero point energy. Apart from λ_0 or ω_0 all the terms on the right hand side of Eq. (1) are given directly by the moments of the eigenvalues of the secular equation for the molecular vibrations. These are related to the widely used Wilson $\boldsymbol{F}$ and $\boldsymbol{G}$ matrices through the relations [2]

$$\sum_{k}^{3n-6} \lambda_k{}^n = \sum_{i}^{3n-6} (\boldsymbol{H}^n)_{ii} = \sum_{i}^{3n-6} ((\boldsymbol{GF})^n)_{ii} \tag{2}$$

which follow from

$$\boldsymbol{H}^n\,\boldsymbol{A}_k = \lambda_k{}^n\,\boldsymbol{A}_k\,. \tag{3}$$

The components of the vector $\boldsymbol{A}_k$ give the transformation of the coordinate system used in the definition of the $\boldsymbol{G}$ and $\boldsymbol{F}$ matrices to normal coordinates.

The advent of high speed computers provides a facile and accurate method for the numerical calculation of the eigenvalues, λ_k, for a polyatomic molecule. Any interest in a method such as Eq. (1) then must come from the physical insight which it can provide. An example of the latter was the derivation of the Bernstein parabolic rule for a constitutive property [3, 4]

$$P_{CX_{4-n}Y_n} = P_{CX_4} + \frac{n}{4}(P_{CY_4} - P_{CX_4} + 8\,\Delta_{XY}) - \frac{n^2\,\Delta_{XY}}{2} \tag{4}$$

Truncation of Eq. (1) at $p = 2$ served to evaluate

$$\Delta_{XY} = 3\alpha/\omega_0 \tag{5}$$

when P is the zero point energy and X and Y are isotopes of the same element [1]. The quantity α introduces no new parameters beyond λ_0 and is related to the masses of X and Y, and the a_{XY} cartesian force constant by [1]

$$\alpha = (1/12\lambda_0)\,(m_X{}^{-1} - m_Y{}^{-1})m_X{}^{-1}\,a_{XY}{}^2\,. \tag{6}$$

Similar to the linear law for the zero point energies of isotopic homologues, there exists the equivalence law for isotopic isomers [1, 5, 6]. The usefulness of the Taylor series expansion method for the zeropoint energy would be increased if one could find systematic methods for the choice of λ_0 which are related to the $\boldsymbol{G}$ and $\boldsymbol{F}$ matrices and which are consistent with the convergence requirement.

Mean Characteristic Eigenvalue

One can write an equation identical to Eq. (1) for each individual eigenvalue. The value of λ_0 which gives convergence for λ_{max}, the maximum eigenvalue, will also give convergence for all eigenvalues, since $o < \lambda_k < \lambda_{max}$ for stable molecules. But λ_{max} is less than either the row sum or column sum of the $\boldsymbol{H}$ matrix.

$$\lambda_{max} \leq \sum_i h_{ij} ,$$
$$\lambda_{max} \leq \sum_j h_{ij} .$$

We are thus led to define the minimax λ, λ_{01}

$$\lambda_{01} = \tfrac{1}{2} \min [\max \sum_i h_{ij} , \max \sum_j h_{ij}] .$$

The minimax λ_{01} guarantees the convergence of (1) through the requirement $o < \lambda_k/\lambda_0 < 2$. Thus the definition of λ_{01} plays a similar role in the relationship of the zero point energy to the $\boldsymbol{F}$ and $\boldsymbol{G}$ matrices as it does in the PEEP method for the evaluation of reduced partition functions [7].

If the $\boldsymbol{H}$ matrix is a diagonal matrix, i. e. we are using normal coordinates, then the minimax definition of λ_0 becomes

$$\lambda_{02} = \tfrac{1}{2} \max h_{ii} .$$

If the coordinate system chosen has small off diagonal elements in the $\boldsymbol{H}$ matrix, e. g. internal coordinates, then the definition of λ_{02} will not differ much from λ_{01} and we expect these λ_0's to give similar convergence properties.

We shall now investigate an interesting property of the $p = 2$ term when an equation similar to Eq. (1) is written for the zero point energy difference between two polyatomic molecules with a common λ_0. The $p=2$ term is $(\hbar\,\omega_0/2)\,(-1\,|\,8)\,[\Sigma\,\delta\lambda^2/\lambda_0 - 2\,\Sigma\delta\lambda/\lambda_0]$ where $\delta\lambda_i = \lambda_i' - \lambda_i$ and $\delta\lambda_i^2 = \lambda i'^2 - \lambda_i^2$.
If λ_0 is defined as

$$\lambda_{03} = \Sigma\,\delta\lambda_i^2 \,|\, 2\Sigma\delta\lambda_i$$

then the $p = 2$ will vanish identically for $\Delta\varepsilon_0 = \tfrac{1}{2}\hbar\,\Sigma\,(\omega_i' - \omega_i)$. Such a series will have interesting convergence properties. We now investigate the convergence of the series related to λ_{03}. The sums $\Sigma\delta\lambda_i^2$ and $\Sigma\delta\lambda_i$ can be given explicitly through the use of cartesian force constants and atomic masses [8]. The convergence requirement for $\Delta\varepsilon_0$ is

$$\sum \frac{\delta\lambda_i}{\lambda_{03}} = \frac{2(\Sigma\delta\lambda_i)^2}{\Sigma\delta\lambda_i^2} < 2 .$$

But

$$(\Sigma\delta\lambda_i)^2 = (\mu_i' - \mu_i)^2\, \boldsymbol{a}_{ii} \cdot \boldsymbol{a}_{ii},$$
$$\Sigma\delta\lambda_i^2 = (\mu_i'^2 - \mu_i^2)\, \boldsymbol{a}_{ii} \cdot \boldsymbol{a}_{ii} + 2\,(\mu_i' - \mu_i)\,\Sigma\mu_j\, \boldsymbol{a}_{ij}^2.$$

Since

$$2\,(\mu_i' - \mu_i)\,\Sigma\mu_j \cdot \boldsymbol{a}_{ij}^2 \text{ is positive}$$
$$\Sigma\delta\lambda_i^2 \geq (\mu_i'^2 - \mu_i^2)\, \boldsymbol{a}_{ii} \cdot \boldsymbol{a}_{ii}$$

Thus

$$\Sigma\delta\lambda_i/\lambda_{01} \leq 2(\mu'-\mu)/(\mu'+\mu) = 2(m-m')/(m+m') .$$

But $(m-m')/(m+m') < 1$ since $m > m'$. Therefore the definition $\lambda_{0\,3}$ suffices for the convergence of $\Delta\varepsilon_0$.

On the other hand the definition $\lambda_0 = \Sigma\lambda_i^2/2\Sigma\lambda_i$ does *not* lead to the convergence of ε_0. This follows directly from

$$\Sigma\lambda_i/\lambda_0 = 2\,(\Sigma\lambda_i)^2/\Sigma\lambda_i^2 < 2 \text{ and } \Sigma\lambda_i^2 = \Sigma\boldsymbol{H}^2{}_{ii} ,$$
$$(\Sigma\lambda_i)^2 = (\Sigma\boldsymbol{H}_{ii})\,(\Sigma\boldsymbol{H}_{ii}) = \Sigma\boldsymbol{H}_{ii}^2 + 2\Sigma\boldsymbol{H}_{ii}\boldsymbol{H}_{jj} .$$

The definition λ_{03} leads to a rather naturally anticipated value for a system of isotopic diatomic molecules.

$$\lambda_{03}\ (\text{diatomic}) = \tfrac{1}{2}\,(\lambda' + \lambda).$$

We are now led to suggest two additional definitions of λ_0 which are related to λ_{03} by successive neglect of off diagonal elements.

$$\lambda_{04} = \delta\Sigma\,(H_{ii})^2/2\delta\Sigma H_{ii} ,$$
$$\lambda_{05} = \Sigma\,(G_{ij}'^2 - G_{ij}^2)\,F_{ij}^2/2\Sigma\,(G'_{ij} - G_{ij})F_{ij} .$$

We have proven the convergence of λ_{03} without exclusion of off diagonal elements. Even in that case, λ_{03} could be decreased by a factor of 2 without leading to divergence. It has been found that off diagonal elements contribute of the order of 10–20 % to $\Sigma\delta\lambda_i$ and $\Sigma\delta\lambda_i^2$ for hydrogen-deuterium substitution[9]. Thus the convergence proof of λ_{03} ist adequate to establish convergence with λ_{04} and λ_{05} when internal coordinates are used for the construction of the $\boldsymbol{F}$ and $\boldsymbol{G}$ matrices.

The definition λ_{05} has an interesting physical interpretation. It represents a mean of the sums of the eigenvalues of the two isotopic molecules, weighting each $\boldsymbol{H}_{ii}$ element by the amount it contributes to $\Sigma\delta\lambda$. The weighting factor is $(\boldsymbol{G}'_{ij} - \boldsymbol{G}_{ij})\boldsymbol{F}_{ij}$.

Convergence Properties

The general convergence features of Eq. (1) have been studied previously [5]. If $X > 1$, then the series oscillates. If $X < 1$, it approaches the limit monotonically. Whether the series for the zero point energy difference will oscillate for a polyatomic molecule will depend on the relative contribution of high and low frequencies to $\Delta\varepsilon_0$. Explicit calculations have been given for the isotopic H_2 and CH_4 molecules [5]. We shall compare the convergence properties of $\lambda_{01} - \lambda_{05}$ for the isotopic methanes in Tables I–VII. All values are calculated with the Jones-McDowell **F** and **G** matrices [10].

Table I. Exact Harmonic Zero Point Energy Differences of the Isotopic Methanes.

Isotopic Pair	ΔZPE (cm^{-1})
CH_4-CH_3D	646.38
CH_3-CH_2D_2	657.01
CH_2D_2-CHD_3	667.38
CHD_3-CD_4	677.13
CH_3D-CHD_4	1324.39
CH_4-CD_4	2647.90

Table II. Taylor Series Expansion of the Zero Point Energy Differences of the Isotopic Methanes [5].

$\nu_0 \leq (2\pi)^{-1} (\lambda_{max}/2)^{\frac{1}{2}} = 2250\ cm^{-1}$

100 [ΔZPE (p) − ΔZPE(exact)]/ΔZPE(exact)

Isotopic Pair	P = 1	2	3	4	5	6
CH_4-CH_3D	0.14	−13.44	−0.60	−4.76	0.13	−2.15
CH_3D-CH_2D_2	−1.53	−14.53	−1.64	−5.48	−0.48	−2.57
CH_2D_2-CHD_3	−3.06	−15.52	−2.55	−6.09	−1.00	−2.91
CHD_2-CD_4	−4.45	−16.40	−3.36	−6.60	−1.43	−3.17

Table III. Taylor Series Expansion of the Zero Point Energy Differences of the Isotopic Methanes.

$\nu_{01} = (2\pi)^{-1} (1/2 \min [\max (\sum H_{ij}), \max (\sum H_{ji})])^{\frac{1}{2}}$

100 (ΔZPE (p) − ΔZPE(exact))/ΔZPE(exact)

Isotopic Pair	ν_0	P = 1	2	3	4	5	6
CH_4-CH_3D	2222	1.40	−13.98	0.24	−5.18	0.74	−2.53
CH_3D-CH_4D_2	2211	0.23	−15.29	−0.41	−6.06	0.42	−3.10
CH_2D_2-CHD_3	2199	−0.80	−16.49	−0.92	−6.84	−0.24	−3.62
CHD_3-CD_4	2187	−1.70	−17.58	−1.28	−7.53	0.19	−4.08

Table IV. Taylor Series Expansion of the Zero Point Energy Differences of the Isotopic Methanes.

$\nu_{02} = (2\pi)^{-1} (1/2 \max (H_{ii}))^{\frac{1}{2}} = 2230.6$

100 (ΔZPE (p) − ΔZPE(exact))/ΔZPE(exact)

Isotopic Pair	P = 1	2	3	4	5	6
CH_4-CH_3D	1.03	−13.81	−0.02	−5.05	0.55	−2.40
CH_3D-CH_2D_2	−0.67	−14.89	−1.06	−5.73	−0.07	−2.79
CH_2D_2	−2.21	−15.86	−1.97	−6.33	−0.58	−3.12
CHD_3	−3.62	−16.72	−2.77	−6.82	−1.00	−3.37

Table V. Taylor Series Expansion of the Zero Point Energy Differences of the Isotopic Methanes.

$\nu_{03} = (2\pi)^{-1} [1/2 \sum \delta\lambda_i^2/\delta\lambda_i]^{\frac{1}{2}}$

100 (ΔZPE (p) − ΔZPE(exact))/ΔZPE(exact)

Isotopic Pair	ν_0	P = 1	2	3	4	5	6
CH_4-CH_3D	2537	−11.18	−11.18	−5.65	−4.23	−2.66	−1.91
CH_4D-CH_2D_2	2530	−12.42	−12.42	−6.67	−5.11	−3.38	−2.50
CH_2D_2-CHD_3	2523	−13.54	−13.54	−7.57	−5.89	−3.99	−3.00
CHD_3-CD_4	2516	−14.54	−14.54	−8.36	−6.54	−4.49	−3.40

Table VI. Taylor Series Expansion of the Zero Point Energy Differences of the Isotopic Methanes.

$\nu_{04} = (2\pi)^{-1}\,[1/2\;\delta\sum H_{ii}^2/\delta\sum H_{ii}]^{\frac{1}{2}}$

		100 (ΔZPE (p) − ΔZPE(exact))/ΔZPE(exact)					
				P			
Isotopic Pair	ν_0	1	2	3	4	5	6
CH_6-CH_3D	2526	−10.80	−11.18	−5.53	−4.19	−2.60	−1.87
CH_3D-CH_2D_2	2521	−12.11	−12.42	−6.57	−5.08	−3.32	−2.47
CH_2D_2-CHD_3	2516	−13.29	−13.54	−7.49	−5.85	−3.94	−2.97
CHD_3-CD_4	2510	−13.07	−13.26	−8.29	−5.11	−3.02	−1.92
CH_3D-CHD_3	2518	−12.71	−12.98	−7.04	−5.47	−3.63	−2.72
CH_4-CD_4	2518	−12.66	−12.94	−6.99	−5.43	−3.54	−2.68

Table VII. Taylor Series Expansion of the Zero Point Energy Differences of the Isotopic Methanes.

$\nu_{05} = (2\pi)^{-1}\,[1/2/\delta\sum G_{ij}{}^2F_{ii}{}^2/\delta\sum H_{ii}]^{\frac{1}{2}}$

		100 (ΔZPE (p) − ΔZPE(exact))/ΔZPE(exact)					
				P			
Isotopic Pair	ν_0	1	2	3	4	5	6
CH_4-CH_3D	2521	−10.60	−11.19	−5.47	−4.17	−2.57	−1.85
CH_3D-CH_2D_2	2517	−11.97	−12.42	−6.53	−5.06	−3.30	−2.45
CH_2D_2-CHD_3	2513	−13.21	−13.54	−7.46	−5.84	−3.93	−2.96
CHD_3-CD_4	2510	−14.33	−14.54	−8.28	−6.51	−4.45	−3.37
CH_3D-CHD_3	2515	−12.60	−12.98	−7.00	−5.41	−3.61	−2.71
CH_4-CD_4	2515	−12.55	−12.95	−6.96	−5.45	−3.57	−2.67

We note by comparison of Tables III and IV and V, VI and VII respectively that the off diagonal elements have little effect on the value of λ_0 and the convergence properties. When $\lambda_i < \lambda_{max}$ the series oscillates. On the other hand when the $p = 2$ term is set at or near zero (λ_{03}, λ_{04}, λ_{05}) the series is a monotonic one.

In the use of Eq. (1) it is advantageous to choose a separate λ_0 for each common symmetry type. We illustrate this by the calculation of the zero point energy differences of the isotopic ethylenes in Table VIII and the isotopic benzenes in Table IX. The common symmetry classes are the planar and non-planar ones. The $\boldsymbol{F}$ and $\boldsymbol{G}$ matrices for ethylene and benzene are those from ARNETT and CRAWFORD [11] and MILLER and CRAWFORD [12] respectively.

Table VIII. Zero-Point Energy Differences of the Isotopic Ethylenes.

$\nu_{03} = (2\pi)^{-1}\,[1/2\;\sum\delta\lambda_i{}^2/\sum\delta\lambda_i]^{\frac{1}{2}}$

	Exact			P				
Isotopic Pair	Value cm^{-1}	ν_0	1	2	3	4	5	6
A) Planar modes								
C_2H_4-C_2H_3D	560.06	2536.6	−12.43	−12.43	−7.82	−6.32	−4.80	−3.89
C_2H_3D-cis $C_2H_2D_2$	561.59	2525.7	−12.30	−12.30	−7.75	−6.29	−4.80	−3.91
C_2H_3D-gem $C_2H_2D_2$	563.11	2529.6	−12.67	−12.67	−8.01	−6.43	−4.88	−3.91
C_2H_3D-trans $C_2H_2D_2$	561.20	2534.3	−12.53	−12.53	−7.88	−6.35	−4.81	−3.89
cis $C_2H_2D_2$-C_2HD_3	564.12	2527.4	−12.75	−12.75	−8.06	−6.45	−4.88	−3.90
gem $C_2H_2D_2$-C_2HD_3	562.61	2523.4	−12.37	−12.37	−7.80	−6.31	−4.80	−3.90
trans $C_2H_2D_2$-C_2HD_3	564.51	2518.7	−12.51	−12.51	−7.93	−6.38	−4.87	−3.92
C_2HD_3-C_2D_4	565.42	2516.4	−12.57	−12.57	−7.97	−6.40	−4.87	−3.91
B) Non-Planar modes								
C_2H_4-C_2H_3D	83.84	903.2	−0.73	−0.73	−0.03	−0.02	0.00	
C_2H_3D-cis $C_2H_2D_2$	86.07	881.8	−0.96	−0.96	−0.03	−0.04	0.00	
C_2H_3D-gem $C_2H_2D_2$	84.57	900.7	−1.32	−1.32	−0.05	−0.06	0.00	
C_2H_3D-trans $C_2H_2D_2$	88.97	857.0	−1.40	−1.40	−0.05	−0.06	0.00	
cis-$C_2H_2D_2$-CHD_3	89.35	854.3	−1.52	−1.52	0.00	−0.06	0.00	
gem $C_2H_2D_2$-C_2HD_3	90.85	834.4	−0.84	−0.84	0.00	−0.03	0.00	
trans-$C_2H_2D_2$-C_2HD_3	86.46	879.3	−1.12	−1.12	−0.02	−0.03	0.00	
C_2HD_3-C_2D_4	91.03	831.6	−0.70	−0.70	−0.03	−0.02	0.00	

Table IX. Zero Point Energy Differences of the Isotopic Benzenes.

$\nu_{03} = (2\pi)^{-1} [1/2 \sum\delta\lambda_i^2/\sum\delta\lambda_i]^{\frac{1}{2}}$

Isotopic Pair	Exact Value cm^{-1}	ν_0	P 1	2	3	4	5	6
A) Planar modes								
C_6H_6-C_6H_5D	582.0	2510	-14.47	-14.47	-9.40	-7.60	-5.80	-4.67
C_6H_5D-o-$C_6H_4D_2$	582.2	2510	-14.50	-14.50	-9.43	**-7.62**	-5.83	-4.69
C_6H_5D-m-$C_6H_4D_2$	582.1	2510	-14.48	-14.48	-9.41	-7.61	-5.81	-4.68
C_6H_5D-p-$C_6H_4D_2$	582.1	2510	-14.48	-14.48	-9.40	-7.60	-5.81	-4.68
o-$C_6H_4D_2$-v-$C_6H_3D_3$	582.3	2510	-14.51	14.51	-9.44	-7.63	-5.84	-4.70
o-$C_6H_4D_2$-a-$C_6H_3D_3$	582.2	2510	-14.49	-14.49	-9.42	-7.61	-5.82	-4.69
o-$C_6H_4D_2$-s-$C_6H_3D_3$	582.1	2510	-14.48	-14.48	-9.40	-7.60	-5.81	-4.68
m-$C_6H_4D_2$-v-$C_6H_3D_3$	582.4	2510	-14.53	-14.53	-9.46	-7.65	-5.85	-4.71
m-$C_6H_4D_2$-a-$C_6H_3D_3$	582.3	2510	-14.51	-14.51	-9.43	-7.63	-5.84	-4.70
m-$C_6H_4D_2$-s-$C_6H_3D_3$	582.2	2510	-14.49	-14.49	-9.42	-7.62	-5.82	-4.69
p-$C_6H_4D_2$-v-$C_6H_3D_3$	582.4	2510	-14.53	-14.53	-9.46	-7.65	-5.86	-4.72
p-$C_6H_4D_2$-a-$C_6H_3D_3$	582.3	2510	-14.51	-14.51	-9.44	-7.63	-5.84	-4.70
p-$C_6H_4D_2$-s-$C_6H_3D_3$	582.2	2510	-14.50	-14.50	-9.42	-7.62	-5.83	-4.69
v-$C_6H_3D_3$-o-$C_6H_2D_4$	582.4	2510	-14.52	-14.52	-9.44	-7.64	-5.84	-4.71
v-$C_6H_3D_3$-m-$C_6H_2D_4$	582.2	2510	-14.50	-14.50	-9.43	-7.62	-5.83	-4.70
v-$C_6H_3D_3$-p-$C_6H_2D_4$	582.2	2510	-14.49	-14.49	-9.42	-7.62	-5.83	-4.69
a-$C_6H_3D_3$-o-$C_6H_2D_4$	582.5	2510	-14.54	-14.54	-9.47	-7.66	-5.86	-4.72
a-$C_6H_3D_3$-m-$C_6H_2D_4$	582.4	2510	-14.52	-14.52	-9.45	-7.64	-5.85	-4.71
a-$C_6H_3D_3$-p-$C_6H_2D_4$	582.4	2510	-14.52	-14.52	-9.44	-7.64	-5.84	-4.71
s-$C_6H_3D_3$-o-$C_6H_2D_4$	582.6	2510	-14.55	-14.55	-9.48	-7.67	-5.87	-4.73
s-$C_6H_3D_3$-m-$C_6H_2D_4$	582.5	2510	-14.53	-14.53	-9.46	-7.66	-5.86	-4.72
s-$C_6H_3D_3$-p-$C_6H_2D_4$	582.4	2510	-14.53	-14.53	-9.46	-7.65	-5.86	-4.72
o-$C_6H_2D_4$-C_6HD_5	582.4	2510	-14.53	-14.53	-9.45	-7.65	-5.85	-4.72
m-$C_6H_2D_4$-C_2HD_5	582.5	2510	-14.54	-14.54	-9.47	-7.66	-5.86	-4.73
p-$C_6H_2D_4$-C_6HD_5	582.6	2510	-14.55	-14.55	-9.48	-7.67	-5.87	-4.73
C_6HD_5-C_6D_6	582.6	2510	-14.55	-14.55	-9.48	-7.67	-5.87	**-4.74**
B) Non-Planar Modes								
C_6H_6-C_6H_5D	106.9	796.6	-6.52	-6.52	-2.30	-1.93	-1.08	-0.84
C_6H_5D-o-$C_6H_4D_2$	107.1	792.1	-6.17	-6.17	-2.43	-1.87	-1.11	-0.82
C_6H_5D-m-$C_6H_4D_2$	106.9	796.5	-6.54	-6.54	-2.32	-1.93	-1.07	-0.81
C_6H_5D-p-$C_6H_4D_2$	107.0	795.7	-6.49	-6.49	-2.31	-2.03	-1.20	-0.96
o-$C_6H_4D_2$-v-$C_6H_3D_3$	107.2	792.0	-6.20	-6.20	-2.45	-1.87	-1.10	-0.81
o-$C_6H_4D_2$-a-$C_6H_3D_3$	107.0	795.6	-6.51	-6.51	-2.32	-2.02	-1.19	-0.93
o-$C_6H_4D_2$-s-$C_6H_3D_3$	106.8	800.9	-6.94	-6.94	-2.25	-1.97	-1.03	-0.78
m-$C_6H_4D_2$-v-$C_6H_3D_3$	107.3	787.5	-5.81	-5.81	-2.60	-1.80	-1.15	-0.81
m-$C_6H_4D_2$-a-$C_6H_3D_3$	107.2	791.1	-6.13	-6.13	-2.44	-1.97	-1.23	-0.94
m-$C_6H_4D_2$-s-$C_6H_3D_3$	107.0	796.5	-6.57	-6.57	-2.34	-1.93	-1.06	-0.79
p-$C_6H_4D_2$-v-$C_6H_3D_3$	107.3	788.4	-5.87	-5.87	-2.60	-1.70	-1.02	-0.67
p-$C_6H_4D_2$-a-$C_6H_3D_3$	107.1	792.0	-6.19	-6.19	-2.45	-1.87	-1.10	-0.80
p-$C_6H_4D_2$-s-$C_6H_3D_3$	106.9	797.4	-6.63	-6.63	-2.35	-1.83	-0.93	-0.65
v-$C_6H_4D_2$-o-$C_6H_3D_3$	107.2	791.0	-6.16	-6.16	-2.45	-1.96	**-1.21**	-0.92
v-$C_6H_4D_2$-m-$C_6H_3D_3$	107.1	795.5	-6.54	-6.54	-2.33	-2.02	-1.17	-0.91
v-$C_6H_4D_2$-p-$C_6H_3D_3$	107.1	794.6	-6.47	-6.47	-2.31	-2.10	**-1.29**	-1.05
a-$C_6H_4D_2$-o-$C_6H_3D_3$	107.4	787.4	-5.84	-5.84	-2.61	-1.79	-1.13	-0.79
a-$C_6H_4D_2$-m-$C_6H_3D_3$	107.2	791.9	-6.22	-6.22	-2.47	-1.87	-1.08	-0.78
a-$C_6H_4D_2$-p-$C_6H_3D_3$	107.2	791.0	-6.15	-6.15	-2.45	-1.96	-1.21	-0.92
s-$C_6H_4D_2$-o-$C_6H_3D_3$	107.6	782.0	-5.38	-5.38	-2.78	-1.79	-1.34	-0.92
s-$C_6H_4D_2$-m-$C_6H_3D_3$	107.4	786.5	-5.78	-5.78	-2.60	-1.89	-1.27	-0.93
s-$C_6H_4D_2$-p-$C_6H_3D_3$	107.5	785.6	-5.70	-5.70	-2.59	-1.98	-1.40	-1.06
o-$C_6H_4D_2$-C_6HD_5	107.3	791.0	-6.19	-6.19	-2.46	-1.95	-1.19	-0.90
m-$C_6H_4D_2$-C_6HD_5	107.5	786.4	-5.80	-5.80	-2.61	-1.87	-1.24	-0.90
p-$C_6H_4D_2$-C_6HD_5	107.4	787.3	-5.87	-5.87	-2.62	-1.78	-1.12	-0.77
C_6HD_5-C_6D_6	107.5	786.4	-5.83	-5.83	-2.61	-1.86	-1.22	-0.88

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