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Spectroscopic Studies on Molecular Vibrations and Coriolis Coupling in Acetylenes, Diiodoacetylene, and Cyanogen

J. BRUNVOLL and S. J. CYVIN

Institutt for teoretisk kjemi, Norges tekniske högskole, Trondheim, Norway

Spectroscopic calculations are reported for some linear symmetrical X_2Y_2 type molecules. For diiodoacetylene the following quantities are given numerically:

(*a*) Force constants,
(*b*) mean-square amplitude matrix elements,
(*c*) parallel and perpendicular mean-square amplitudes,
(*d*) mean amplitudes of vibration,
(*e*) Bastiansen—Morino shrinkage effects,
(*f*) L-matrix elements, and
(*g*) Coriolis coupling coefficients.

The calculated L-matrix elements and Coriolis coupling coefficients are also given for acetylene, acetylene-d_4, and cyanogen.

Our studies on mean amplitudes of vibration [1] and Bastiansen—Morino shrinkage effects [2] in linear molecules [3–5] have been continued by the presently reported study on diiodoacetylene. This molecule is of the same type as cyanogen [3] and acetylene [4], *viz.* linear symmetrical X_2Y_2 (symmetry group $D_{\infty h}$). The work has been actuated by the scheduled electron-diffraction study on diiodoacetylene (Bastiansen *et al.*).

In addition to the mean amplitudes of vibration, shrinkage effects and related quantities, the Coriolis coupling coefficients [6,7] of linear symmetrical X_2Y_2 type molecules have been studied [8]. In the present work numerical ζ-values are reported for acetylene, acetylene-d_4, diiodoacetylene, and cyanogen.

DIIODOACETYLENE

Experimental data. We used the experimental vibrational frequencies from Cleveland and Meister,[9,10] *viz.* (Σ_g^+:) 191, 2109, (Σ_u^+:) 710, (Π_g:) 310, and (Π_u:) 115, all in cm^{-1}. As equilibrium distances we had to use the old data [11] of (C≡C) $D = 1.18$ Å, and (C—I) $R = 2.03$ Å because of the lack of more recent

Table 1. Force constants and mean-square amplitude matrix elements for diiodoacetylene*

Symbol	Force constant (mdyne/Å)	Symbol	Mean-square amplitude (Å²) $T = 0$	298 °K
F_1	2.78201	Σ_1	0.00130947	0.00215282
F_2	15.799	Σ_2	0.00133440	0.00133775
F_{12}	1.03984	Σ_{12}	−0.00090594	−0.00085365
F_3	3.25579	Σ_3	0.00216567	0.00231121
F_4	0.058986	Σ_4	0.0521920	0.0823290
F_5	0.146943	Σ_5	0.00777209	0.0287251

* For explanation of symbols, see Refs.[3,4]

measurements. The same data have also been applied by Cleveland and Meister [9], and are hoped to be sufficiently accurate for our purpose.

Force constants. The considered model contains six harmonic force constants, whereas the number of vibrational frequencies is five. Since no data on different isotopic molecules are available in the present case, one assumption must be made in order to calculate the force constants from the frequencies. Cleveland and Meister [9] transferred the force constant of CC stretching from methyliodoacetylene. This assumption seems to be very reasonable, and we followed the same procedure, putting F_2 equal to 15.799 mdyne/Å. The presently recalculated force constants are given in Table 1. The calculations confirm the results of Cleveland and Meister [9], as the small differences certainly may be ascribed to slightly different physical constants. We used $\mu_C = 0.0833065$ (based on C^{12}) and $\mu_I = 0.0078790$ $(\text{Amu})^{-1}$ for the inverse masses of the C and I atoms, respectively. The squared wave numbers (ω in cm^{-1}) were converted to λ values (in mdyne/ÅAmu^{-1}) by the factor 0.0588932 ($\lambda = 4\pi^2c^2\omega^2$). In Table 1 the force field is given in terms of the symmetrized force constants. They are based on a set of symmetry coordinates, which have been specified elsewhere [3]. To compare our result with that of Cleveland and Meister [9], we performed the transformation of our force constants to those in the notation of the mentioned investigators. The result is given in the following.

$$\begin{aligned}
k_a &= F_2 &&= 15.799 \quad (15.799)\\
k_i &= (1/2)(F_1 + F_3) &&= 3.0189 \quad (3.0186)\\
k_\varphi &= (D/2R)(F_4 + F_5) &&= 0.059851 \quad (0.05967)\\
k_{ia} &= 2^{-1/2}F_{12} &&= 0.73528 \quad (0.7350)\\
k_{\varphi\varphi} &= (D/2R)(F_5 - F_4) &&= 0.025564 \quad (0.02538)\\
k_{ii} &= (1/2)(F_1 - F_3) &&= -0.23689 \quad (-0.2372)
\end{aligned}$$

The values from Cleveland and Meister are given in parentheses. r_i and r_a in the notation of Cleveland and Meister corresponds to our R and D, respectively.

Mean-square amplitude matrix. The Σ-matrix elements have been determined by means of the relation [12]

$$\Sigma = \mathbf{L}\,\Delta\,\tilde{\mathbf{L}}$$

and are included in Table 1.

Table 2. Mean-square parallel (σ) and perpendicular (τ) amplitudes for diiodoacetylene at $T = 0$ and 298 °K

Distance	Symbol	Generalized mean-square amplitudes ($Å^2$ units) $T = 0$	298 °K
C−I	σ_r	0.00173757	0.00223201
	τ_r	0.00759139	0.0261377
C≡C	σ_d	0.00133440	0.00133775
	τ_d	0.00901976	0.0142280
C...I	σ_{r+d}	0.00179077	0.00236251
	τ_{r+d}	0.00884521	0.0281155
I...I	σ_{2r+d}	0.00139095	0.00322888
	τ_{2r+d}	0.00000409	0.00000645

Table 3. Mean amplitudes of vibration and shrinkage effects for diiodoacetylene

Distance	Symbol	Mean amplitude of vibration (Å) $T = 0$	298 °K
C−I	u_r	0.0417	0.0472
C≡C	u_d	0.0365	0.0366
C...I	u_{r+d}	0.0423	0.0486
I...I	u_{2r+d}	0.0373	0.0568
Distance	**Symbol**	**Shrinkage effect (Å) $T = 0$**	**298 °K**
C...I	δ^g_{r+d}	0.0086	0.0162
I...I	δ^g_{2r+d}	0.0151	0.0378

The mean-square parallel and perpendicular amplitudes (σ and τ, respectively) are defined for the here considered molecular model in Ref.[3], where these quantities are given in terms of the Σ-matrix elements. They are given numerically for diiodoacetylene in Table 2.

Mean amplitudes of vibration and shrinkage effects. The calculated mean amplitudes of vibration (u) and Bastiansen-Morino shrinkage effects (δ) for diiodoacetylene are reported in Table 3.

L-Matrices

Because of the wide applicability of the normal coordinate transformation matrix, L (S = L Q), it seems justified to specify its elements for the presently considered molecules. The L-matrix has been used in the present computations on diiodoacetylene (*cf.* the Σ-matrix above), as well as in our previous computations on acetylene [4], and cyanogen [3]. The L-matrix elements from our calculations are given numerically for acetylene, acetylene-d_4, diiodoacetylene, and cyanogen in the following. Units: $\text{Amu}^{-1/2}$.

Acetylene.

$$L_{11} = 0.774617 \qquad L_{12} = -0.689355$$
$$L_{21} = 0.175761 \qquad L_{22} = 0.368403$$
$$L_{33} = 1.036939 \qquad L_{44} = 1.360063 \qquad L_{55} = 1.106234$$

Acetylene-d_4.

$$L_{11} = 0.279561 \qquad L_{12} = -0.708168$$
$$L_{21} = 0.294525 \qquad L_{22} = 0.282609$$
$$L_{33} = 0.761351 \qquad L_{44} = 1.133903 \qquad L_{55} = 0.812230$$

Diiodoacetylene

$$L_{11} = 0.085022 \qquad L_{12} = -0.289752$$
$$L_{21} = 0.005279 \qquad L_{22} = 0.408148$$
$$L_{33} = 0.301969 \qquad L_{44} = 0.979536 \qquad L_{55} = 0.230227$$

Cyanogen

$$L_{11} = 0.383545 \qquad L_{12} = 0.0871179$$
$$L_{21} = -0.353533 \qquad L_{22} = 0.204027$$
$$L_{33} = 0.393315 \qquad L_{44} = 1.120054 \qquad L_{55} = 0.429550$$

Coriolis coupling coefficients

The Coriolis coefficients of rotation-vibration interaction (ζ-values) for the linear symmetrical X_2Y_2 molecular model have been treated theoretically

Table 4. Coriolis coupling coefficients (ζ) in some molecules *

Molecule	ζ_{14}	ζ_{24}
Acetylene	0.436	−0.900
Acetylene-d_4	−0.081	−0.997
Diiodoacetylene	0.056	−0.998
Cyanogen	0.982	−0.189

* Notice the relation [8] $\zeta_{14}^2 + \zeta_{24}^2 = 1$.

elsewhere [8]. There are two different non-trivial (*i.e.* force-constant dependent) ζ-values in the considered case, *viz.*

$$\zeta_{14} = \zeta^{x}{}_{1,4b} = -\zeta^{y}{}_{1,4a}$$
$$\zeta_{24} = \zeta^{x}{}_{2,4b} = -\zeta^{y}{}_{2,4a}$$

They may be calculated again by means of the L-matrix in various ways. We have found the application of [6,7] $\zeta^{a} = \tilde{L}\, G^{-1}\, C^{a}\, \tilde{L}^{-1}$ to be the most useful one of the methods, and we obtained the simple equations:

$$\zeta_{14} = L_{44}^{-1}\,[(D/R)^{1/2}L_{11} - (2R/D)^{1/2}L_{21}]$$
$$\zeta_{24} = L_{44}^{-1}\,[(D/R)^{1/2}L_{12} - (2R/D)^{1/2}L_{22}]$$

The numerical results for the four molecules in question are given in Table 4.

Note The digits as given in this report are not necessarily significant. They have been included to preserve mathematical consistency.

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