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Laser-Induced Fluorescence Study of the S_1 State of Doubly-Substituted Carbon-13 Acetylene and Harmonic Force Field Determination

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Abstract

In the first half of this study, rotational and vibrational structures of six Franck-Condon bright states of S_1 doubly-substituted carbon-13 acetylene are determined from the laser-induced fluorescence spectra of the molecule and an updated geometry of the *trans* conformer of S_1 acetylene is provided. In the second half, we determine the harmonic force constants of S_1 acetylene, which takes into account both diagonal and off-diagonal x_{ij} anharmonicities. Results from previous studies of various isotopologues of the molecule (including the first half of this work), both experimental and theoretical, are used to obtain a set of force constants which agree well with ab initio calculations. Our set of force constants of S_1 acetylene is believed to be more reliable than Tobiasson's previous result [1], which does not include off-diagonal anharmonicities.

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I. INTRODUCTION

The study of the first electronically excited S_1 state of acetylene molecule dates back exactly one hundred years ago, when Stark and Lipp published the first absorption spectrum of gas-phase acetylene from 2200-1900 Å [2]. The major breakthrough occurred in the mid-50's, when Ingold and King [3] and Innes [4] demonstrated that the lowest-lying excited electronic state in the absorption spectrum has a near-prolate top *trans*-bent structure (C_{2h} point group), in contrast to the linear structure in the electronic ground state. From the rotational selection rule, they identified the transition as a C-type $\tilde{A}^1A_u - \tilde{X}^1\Sigma_g$ transition. Since then, the vibrational structure of the *trans* conformer of S_1 acetylene has been nearly completely characterized [5–8] and important dynamics, such as Coriolis and Darling-Dennison resonance [6, 9] and isomerization to the *cis* conformer [10], have been identified. Along with experimental works, ab initio calculations have been carried to treat the *trans* conformer in a global sense and good agreement with experiment has been obtained [11].

Most of the work on S_1 acetylene was done on the naturally-abundant species (hence known as C12). However, in order to fully characterize a molecule, isotopologue information is necessary for the determination of the molecular geometry as well as the harmonic force field, provided that the Born-Oppenheimer approximation is valid. In this paper, the laser induced fluorescence spectra of doubly-substituted carbon-13 acetylene (C13) recorded by Michelle Clark during her PhD work at MIT is reanalyzed and the axis-switching effect has been taken into account, allowing the determination of the A , B , and C rotational constants, as well as band-origins of six Franck-Condon bright states involving mode 2 (CC-stretch) and mode 3 (*trans*-bending). Details of the experiment can be found in Chapter 2 of Clark's PhD thesis [12] and are not repeated here. Combining all previous studies of S_1 acetylene, both experimental [5–8, 13, 14] and theoretical [11], we provide a more reliable set of force constants of S_1 acetylene, to be compared with Tobiason's force field analysis [1], as well as an updated geometry of the molecule. The most significant contribution of our present work is the inclusion of all the x_{ij} anharmonicitys, both diagonal and off-diagonal, to the harmonic frequencies, in addition to the fact that the fundamentals of several normal modes are now much better determined (notably ν_1 of C12 acetylene [8]). This allows us to determine the force constants with less ambiguity compared with previous work [1]. An ongoing project

is to use this updated set of force constants and molecular geometry to refine the S₁-S₀ Franck-Condon calculation.

II. RESULTS

The C-type rotational selection rule $K'_a - l'' = \pm 1$ for the S₁-S₀ electronic transition of acetylene normally prohibits transitions to $K'_a = 0$ and 2 levels from the ground electronic state with zero vibrational angular momentum, $l'' = 0$. For a near prolate top, the diagonal matrix elements of the rotational Hamiltonian are given by (with $K \equiv K_a$ being unsigned and $|k|=K$ being signed) [5]

$$H_{k,k} = T_v + \frac{1}{2}(B + C)(J(J + 1) - k^2) + Ak^2 - D_{JJ}J^2(J + 1)^2 - D_{JK}J(J + 1)k^2 - D_{KK}k^4, \quad (1)$$

and the off-diagonal ones are given by

$$H_{k\pm 2,k} = \frac{1}{4}(B - C)\sqrt{(J^2 - (k \pm 1)^2)((J + 1)^2 - (k \pm 1)^2)}. \quad (2)$$

As a result, only B , C , and D_{JJ} can be determined from a $\Pi - \Sigma$ ($K' = 1 - l'' = 0$ transition) spectrum, since one needs at least two K 's to determine the A constant. However, because of large change of geometry upon excitation to the S₁ state, $K'_a - l'' = 0, \pm 2$ transitions can be weakly allowed [15]. This so-called axis-switching effect can best be understood if one realizes that the molecular wave function normally used is expressed in terms of a molecule-fixed coordinate system instead of a space-fixed coordinate system [15]. In other words, the coordinate system rotates as the geometry of the molecule changes (while in the usual selection rule, a fixed coordinate system is assumed), thus breaking the simple selection rule. This is very similar in essence to the Duschinsky effect, where the coordinates of the vibrational normal modes change upon large geometry change induced by an electronic transition [15, 16].

The result is listed in Table I and line assignments are provided in the Supporting Information. V_n^m is a short-hand notation for a transition from n quanta of the trans-bending mode, ν_4'' of the ground electronic state to m quanta of the trans-bending mode, ν_3' in the excited state. Rotational constants B and C , D_{JJ} , and $T_v + Ak^2$ terms are first determined by assigning the rotational lines of the much stronger $\Pi - \Sigma$ transition. Axis-switching lines from the weaker $\Sigma - \Sigma$ transition can then be easily picked out by noticing that the axis-switching Q(J) line near $J=20$ should lie close to the normal Q(J+1) line. This is because

TABLE I: Rotational and vibrational constants for the observed vibrational states. Units are all in cm^{-1} . Those constants left in blank were not included in the fit. Numbers in the parentheses are $\pm 1\sigma$ uncertainties.

Constants	V_0^0	V_0^1	V_0^2	$2_0^1V_0^0$	$2_0^1V_0^1$	$2_0^1V_0^2$
T_v	42214.49(1)	43250.06(1)	44268.55(1)	43551.43(1)	44586.99(1)	45605.17(3)
A	12.783(13)	13.692(7)	14.811(7)	12.661(9)	13.513(8)	14.340(26)
B	1.0592(1)	1.0610(1)	1.0618(0)	1.0513(1)	1.0522(0)	1.0514(1)
C	0.9750(1)	0.9717(1)	0.9686(0)	0.9679(1)	0.9642(0)	0.9609(1)
$D_{JJ} \times 10^6$	2.30(7)	2.44(7)	1.98(4)	2.6(1)	2.04(4)	2.00(2)
$D_{JK} \times 10^5$		9(2)		7(1)	5(3)	28(9)
D_{KK}	0.004(3)		0.013(2)			
rms	0.021	0.026	0.016	0.017	0.015	0.024

the expected separation of the $K=1f$ and $0f$ levels will be about 8 cm^{-1} at $J=20$, based on information from the study of C12. This also happens to be roughly the spacing of the two Q branches near that J value. Unfortunately, only Q-type transitions are allowed for a $\Sigma - \Sigma$ band because of the parity selection rule, but in general the observed progression of axis-switching Q lines is fitted with good accuracy. This is particularly made possible by the fact that the transition is red-shifted with respect to the $\Pi - \Sigma$ transition. In addition, for an axis-switching transition, the intensities scale approximately as $J^3 \exp[-B''J(J+1)hc/kT]$ [15], whereas the normal rotational intensities scale as $J \exp[-B''J(J+1)hc/kT]$ [15] and thus reach maximum earlier ($B'' = 1.1196 \text{ cm}^{-1}$ is the ground electronic state rotational constant [17]). As a result, the strongest part of the relatively weak $\Sigma - \Sigma$ axis-switching lines avoids being buried under stronger Q lines which reach maximum intensity at around $J=6$ in our experimental conditions. In contrast, all P, Q, and R transitions are allowed for the axis-switching $\Delta - \Sigma$ transition. However, the intensities of these transitions is only about half that of the $\Sigma - \Sigma$ [15], and the band is severely overlapped by the R-head of the $\Pi - \Sigma$ band. As a result, no attempts are made to assign the $\Delta - \Sigma$ transition except for the V_0^0 and V_0^1 bands, mainly due to the fact that those bands were sampled only by relatively short

scans and only a few $\Sigma - \Sigma$ Q lines can be assigned. For those two bands, a progression of Q and/or P branches of the $\Delta - \Sigma$ transition can still be observed. The spectrum in the R-branch region was not recorded. The A rotational constant can thus be determined for all the observed levels. D_{JK} and D_K are added only if they significantly improve the fit and also give reasonable uncertainties. The inclusion of those two constants only causes a small change in the other fitted constants and sometimes even increases the uncertainties of those values. The overall *rms* is good, given the spectra were calibrated to an accuracy of around 0.02 cm^{-1} .

III. ROTATIONAL AND VIBRATIONAL ANALYSIS

As can be seen from Table I, the A and C rotational constants are observed to increase or decrease linearly with the number of quanta in mode 3, with the greatest changes occurring in the values of the A constant. This is consistent with the fact that as more and more quanta of the *trans*-bending mode 3 are excited, the molecule becomes quasi-linear, with an increased apparent value of the A rotational constant [5]. It should be noted that the values of B constant deviate from the linear trend, in particular for the progression containing one quantum of ν_2 . This might be caused by some J-dependent Coriolis-type perturbation. A similar effect has been observed in C_2D_2 [14].

The rovibrational parameters can be determined from the rotational constants by the relation

$$R_v = R_e - \alpha_2^R(\nu_2 + \frac{1}{2}) - \alpha_3^R(\nu_3 + \frac{1}{2}), \quad (3)$$

where R can be either A , B , or C , and ν_2 and ν_3 stand for the number of quanta of those two modes in each level. The result is presented in Table II. Note that R_e here can only be considered an effective value, since not all α 's can be determined from the available data. A weighted fit based on the uncertainties of the fit values is used throughout this work.

With the inclusion of the new C13 rotational constants, geometrical parameters of the *trans* conformer of S_1 acetylene can be updated. Assuming the validity of the Born-Oppenheimer approximation, the equilibrium structure of a molecule should be isotope-independent. In fact, without additional isotopologue information, the equilibrium geometry of a polyatomic molecule cannot generally be determined. For *trans* S_1 acetylene, the

TABLE II: Rotational and vibrational constants of the observed vibrational states. Units are all in cm^{-1} .

$A_e = 12.44(15)$	$B_e = 1.064(1)$	$C_e = 0.9806(3)$
$\alpha_2^A = 0.23(9)$	$\alpha_2^B = 0.0088(6)$	$\alpha_2^C = 0.0075(2)$
$\alpha_3^A = -0.96(6)$	$\alpha_3^B = -0.0009(4)$	$\alpha_3^C = 0.0034(1)$

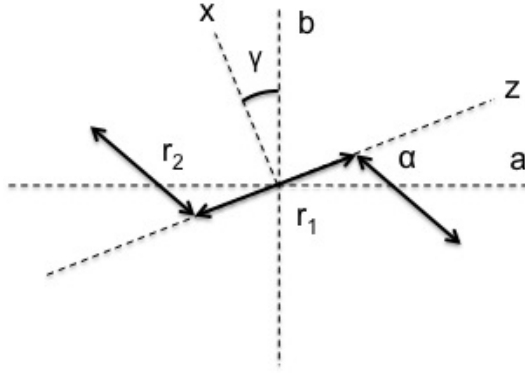


FIG. 1: Geometry of *trans* acetylene (adapted from ref [18]). r_1 and r_2 are the r_{CC} and r_{CH} bond lengths respectively. α is the CCH angle. γ is the angle between the principal axis system and the x, y, z -coordinate system, with the y -axis being out of plane. Note that in the final results, the CCH angle is reported as the supplementary angle of α .

principal moments of inertia are given by the equations [18]

$$\frac{1}{2}I_0^A = \frac{r_1^2}{4}(m_1 + m_2)\sin^2\gamma + m_2r_2^2\sin^2(\gamma - \alpha) + m_2r_1r_2\sin(\gamma - \alpha)\sin\gamma \quad (4)$$

$$\frac{1}{2}I_0^C = \frac{r_1^2}{4}(m_1 + m_2) + m_2r_2^2 + m_2r_1r_2\cos\alpha \quad (5)$$

$$\tan 2\gamma = \frac{m_2r_2^2\sin 2\alpha + m_2r_1r_2\sin\alpha}{\frac{1}{4}(m_1 + m_2)r_1^2 + m_2r_2^2\cos 2\alpha + m_2r_1r_2\cos\alpha}, \quad (6)$$

where m_1 and m_2 are the masses of various isotopes of carbon and hydrogen atoms, respectively. In this study, geometrical parameters are fitted to I_a and I_c of C12, C₂D₂ and C13. As a usual practice, the rotational constants, R_0 , from the ground vibrational state are used, instead of equilibrium rotational constants, mostly because only some of the α_i parameters are known in the S₁ state. It should be noted that attempts have been made to include I_b in the fit as well. However, the fit residuals become larger when I_b is included, possibly due

to the presence of a positive inertial defect, calculated to be $\Delta^\circ = I_c - I_a - I_b \approx 0.06 \text{ amu } \text{\AA}^2$ for all three isotopologues, while I_c is supposed to be equal to $I_a + I_b$ for a planar molecule. The calculated inertial defect, which occurs mainly due to vibration, is consistent with the typical value for a “well-behaved” planer molecule [19]. The inertial defect is not taken into account during the structural determination, thus the geometry we obtain is best described as a zero-point geometry. From the fit, one obtains

$$r_{CC} = 1.374(1)\text{\AA} \quad r_{CH} = 1.099(2)\text{\AA} \quad \angle CCH = 122.82(8)^\circ.$$

The updated structure is not very different from the result in [18] . The most noticeable change is a slight increase (+0.34°) in the CCH bond angle.

From the band origins of the six vibrational levels, harmonic frequencies and anharmonicities can be obtained. However, as no global fit is possible, the result should be treated with care, especially for the harmonic frequencies and T_e (not including the zero-point energy) in Eq.(7). The six levels are fitted to the model

$$G(\nu_2 \nu_3) = T_e + \omega_2(\nu_2 + 1/2) + \omega_3(\nu_3 + 1/2) + x_{22}(\nu_2 + 1/2)^2 + x_{33}(\nu_3 + 1/2)^2 + x_{23}(\nu_2 + 1/2)(\nu_3 + 1/2). \quad (7)$$

It should be mentioned that x_{22} can neither be fitted in our model (since we need at least three different quanta of ν_2 to determine its value) nor absorbed into any of the fitted terms. An approximate value of x_{22} can be obtained by using Eq. (8) in the next section, based on the known x_{22} of C12 [8]. For comparison, a fit result when x_{22} is effectively set to be zero is also reported (see Table III). As expected, the value of ω_2 is the one most affected

TABLE III: Vibrational analysis. Numbers with asterisks are fixed in each fit. Units are all in cm^{-1} .

T_e	41013.8(2)	41021.7(2)
ω_2	1358.1(1)	1337.1(2)
ω_2	1052.9(3)	1052.9(2)
x_{33}	-8.61(8)	-8.60(8)
x_{23}	-0.17(9)	-0.15(10)
x_{22}	-10.86*	0*

by the choice of the x_{22} value. It should be re-emphasized that the “harmonic frequencies” obtained here are not real harmonic frequencies, since no global fit is possible. Thus, the treatment introduced in the next section is still necessary to obtain more accurate harmonic frequencies.

IV. HARMONIC FORCE-FIELD DETERMINATION

As promised, a new harmonic force-field analysis with a complete set of x_{ij} anharmonicities [7–9, 11, 20, 21] can now be completed, with the inclusion of several new fundamental frequencies, notably ν_1 of C12 [8] in combination with the results from the present work. In Tobiasson’s harmonic force field analysis [1], only the diagonal anharmonicities are included, claiming that off-diagonal ones should be relatively small. However, recent developments in the study of acetylene, both experimental and ab initio, have shown that several off-diagonal anharmonicities are much larger than or at least comparable to the diagonal ones, most notably $x_{15}=-158.57 \text{ cm}^{-1}$ [11] and $x_{36}=-33.45 \text{ cm}^{-1}$ [20]. The former is an ab initio (VPT2) anharmonicity between the high-frequency symmetric and asymmetric stretch modes. The large value of the latter is caused by the fact that modes 3 and 6 are the two active modes in the S_1 acetylene *cis* \leftrightarrow *trans* isomerization path [10, 20]. A complete list of anharmonicities can be found in [11], with updated values: $x_{56}=-8.98 \text{ cm}^{-1}$ and $x_{45}=-16.81 \text{ cm}^{-1}$. Only those associated with modes 1 and 5 have not been experimentally determined because it would require observation of very high-lying vibrational levels well above the dissociation limit. However, given excellent agreement of the ab initio fundamental frequencies of those two modes with the experimental values, we have confidence in the calculation. Anharmonicity constants for various isotopologues of S_1 acetylene are very sparsely available and most of them are not very well-determined. An empirical relation [22] is used instead to infer those values from C12 anharmonicities

$$x_{ik}^* = \frac{\omega_i^* \omega_k^*}{\omega_i \omega_k} x_{ik}, \quad (8)$$

where an asterisk indicates the corresponding value for an isotopologue. As the relation involves ratios of harmonic frequencies, and since not all of them are available for various isotopologues (only those of C12 can be determined), ab initio harmonic frequencies are used to obtain anharmonicities of other isotopologues, as ratios of ab initio values are usually of

good quality. Ab initio harmonic frequencies of the isotopologues are generated based on results in [11]. The harmonic frequencies are related to fundamentals and anharmonicities via the relation

$$\omega_i = \nu_i - 2x_{ii} - \frac{1}{2} \sum_{k \neq i} x_{ik}, \quad (9)$$

where ν_i is an observed fundamental frequency (e.g. the difference between the band origin of $\nu_3=1$ and 0), while harmonic frequencies are the second derivative of the potential energy surface along a normal mode direction. For force-constant calculations, harmonic frequencies must be used, because the usual force constants are related to a harmonic force field. The harmonic frequencies are summarized in Table IV.

As can be seen, the harmonic frequencies listed are quite different from the ones that Tobiasson used in his work [1]. Most of them, even those of various isotopologues, agree excellently with ab initio harmonic frequencies, which are known to produce accurate fundamentals. This justifies the use of the empirical relation Eq. (8). The discrepancies for mode 4 and mode 6 can mostly be explained by the choice of coordinate system [11]. In the VPT2 calculations, a rectilinear coordinate system is used, which tends to yield more accurate result for stretching modes and less accurate ones for bending and especially torsional modes [11]. When a curvilinear system is used, a much better agreement with the experiment can be achieved for those two modes. It should be noted that the agreement with the ab initio ω_1 and ω_2 for C_2D_2 is significantly poorer than for other harmonic frequencies. This casts doubt on the accuracy of the observed fundamentals [14], since the stretching mode should be very accurately determined in the ab initio calculation, as is the case for other isotopologues. Using the Teller-Redlich product rule [22], which relates the products of harmonic frequencies of a given symmetry of two different isotopologues to the mass and geometrical structure of the molecule, we have for modes 1, 2, and 3 of $C12$ and C_2D_2

$$\frac{\omega_1\omega_2\omega_3}{\omega_1^*\omega_2^*\omega_3^*} = \frac{m_H^*m_C^*}{m_Hm_C} \sqrt{\frac{I_c}{I_c^*}}, \quad (10)$$

where an asterisk indicates the relevant value for the other isotopologue. It is evident that (Table V) ab initio calculation essentially yields the same ratio as the one calculated from Eq.(10), but the agreement with experimental harmonic frequencies is worse for C_2D_2 . In comparison, if we use the experimental ω_2 and ω_3 of $C13$ to extrapolate to its ω_1 value, it yields a result that is very close to the ab initio value, which is expected to be close to

TABLE IV: Experimental, ab initio, and fit harmonic frequencies. Data in asterisks are not included in the harmonic force field fit. Units are all in cm^{-1} .

	mode	Exp. fundamental	Ab initio harmonic	Exp. harmonic	Fit harmonic	Predicted fundamental
C12	1	2880.1 [8]	3053.5	3052.1	3052.2	2880.1
	2	1386.9 [5]	1424.6	1420.9	1421.0	1387.0
	3	1047.6 [5]	1106.1	1098.0	1098.1	1047.7
	4	764.9 [6]	757.9	787.7	787.7	764.9
	5	2857.4 [7]	3033.4	3032.4	3031.1	2856.1
	6	768.3 [6]	780.6	801.6	800.8	767.5
C2D2 [14]	1	2209.2*	2262.6	2303.5*	2262.3	2168.0
	2	1305.8*	1385.1	1335.3*	1378.0	1348.5
	3	845.3	877.8	875.6	874.0	843.8
	4		556.5		578.4	564.6
	5		2227.2		2225.6	2130.6
	6		573.2		588.0	568.7
C2HD [13]	1		3043.6		3041.8	2893.5
	2	1367.4	1403.7	1399.0	1398.2	1366.6
	3	980.8	1026.1	1021.8	1022.7	981.7
	4		664.8		691.0	672.4
	5		2245.2		2244.2	2131.3
	6	635.7	644.4	660.6	659.5	634.7
C13	1		3043.7		3042.3	2871.4
	2	1336.9	1372.4	1368.9	1369.5	1337.6
	3	1035.6	1093.5	1085.1	1085.0	1035.5
	4		755.6		785.4	763.0
	5		3024.4		3022.0	2848.2
	6		778.3		798.4	765.5

TABLE V: Teller-Redlich product rule for mode 1, 2 and 3.

	Calc.	Ab initio	Exp.
C12/C ₂ D ₂	1.748	1.749	1.768(13)
C12/C13	1.054	1.054	$\omega_3=3043(19)\text{cm}^{-1}$

the experimental value. Indeed, in the original paper on C₂D₂, the ν_2 fundamental was not directly observed; the $\nu_2=1$ level seems to be determined from a combination band with ν_1 , the position of which also might not be securely determined. Considering all these difficulties, the ν_1 and ν_2 fundamentals of C₂D₂ are not included in the harmonic force-field fit. In fact, inclusion of the two corresponding harmonic frequencies makes the fit residual much larger than otherwise. The assignment of ν_3 fundamental [14] should be secure, since a long progression of this Franck-Condon active mode was observed in the study.

Based on harmonic frequencies, harmonic force constants of the *trans* conformer of the S₁ state of acetylene can be determined by the **GF** matrix method. This is a well-developed method to obtain force constants, and has been discussed in great detail in [23], as well as in Tobiasson’s force constant analysis paper [1]. Here, only a brief theoretical background is provided. In the internal coordinate system, harmonic frequencies can be obtained from the secular equation [23]

$$|\mathbf{F} - \mathbf{G}^{-1}\lambda| = 0, \quad (11)$$

where F_{tk} is an element of the force constant matrix, **F**, expressed in internal coordinates, t and k represent specific internal coordinates, \mathbf{G}^{-1} is the inverse of the matrix **G**, which contains geometrical and isotope information of the molecule, and the λ are the squares of the harmonic frequencies. The internal coordinates of acetylene are represented in Fig. 2. The relation in Eq. (11) is analogous to the case of diatomic molecules, where the harmonic frequencies equal to the square root of force constant divided by the reduced mass. Thus, in many ways, the **GF** matrix is the polyatomic version of this relation, with **G** being a reduced mass matrix that also contains geometrical information about the molecule. In fact, **G** can be determined from [23]

$$\mathbf{G} = \mathbf{B}\mathbf{m}^{-1}\mathbf{B}^T, \quad (12)$$

where **B** transforms Cartesian displacement coordinates to internal coordinates and \mathbf{m}^{-1} is

a diagonal inverse mass matrix. \mathbf{G} can also be obtained from a purely geometrical point of view described in [23]. Both methods are used to obtain the \mathbf{G} matrix for the four isotopologues of acetylene. Specific forms of the matrices as well as \mathbf{F} are provided in the Supporting Information. Note that \mathbf{m}^{-1} and thus \mathbf{G} are isotope-dependent, but \mathbf{F} is not isotope-dependent within the Born-Oppenheimer approximation. By simple diagonalization of each \mathbf{GF} matrix, the square-root of the eigenvalues are fitted to the experimental harmonic frequencies listed in Table IV. Our updated acetylene geometry is used in the \mathbf{G} matrices. An uncertainty of 2 cm^{-1} is given for all C12 harmonic frequencies and 5 cm^{-1} for the rest. Note that since mode 4 is the only mode that involves out of plane motion, \mathbf{GF} is automatically block-diagonalized into an 1×1 ω_4 block and a 5×5 block. Such feature is obvious if one uses the geometrical approach to obtain \mathbf{G} and takes the symmetry of different vibrational normal modes into account.

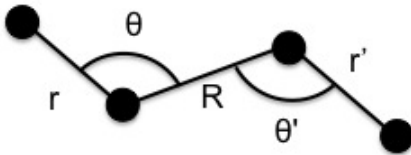


FIG. 2: Internal coordinates of acetylene. Note that the torsional coordinate, τ being out of plane, is not shown.

To increase the accuracy of the fit, we also fit to the a -axis Coriolis constant $\xi_{46}^a = 0.707 \pm 0.006$ between modes 4 and 6 [6]. Details of obtaining ξ_{46}^a from \mathbf{GF} are described in [1]. The matrix \mathbf{L} mentioned there is the one that diagonalizes \mathbf{GF} . Note that there is a typo in Eq. (4) of ref [1]. The summation should be from $i = 1 - 4$, since there are only four atoms in acetylene, and the superscript should specify principal axes a, b , and c . Thus, care should be taken to transform \mathbf{B} into the principal axis system.

We encounter similar fitting problems as noted in Tobiasson's previous work [1]. When we try to fit to all ten parameters, large relative uncertainties are found in F_{rR} and $F_{r'\theta}$, as well as in $F_{r'r'}$. The first two were constrained to be zero in [1]. It turns out that those three force constants are much smaller than the others obtained from the ab initio calculation [11]. We thus also tried constraining the first two parameters to be zero, and reasonable parameter uncertainties are obtained. In addition, given confidence in the accuracy of the VPT2 calculation, we also tried constraining F_{rR} and $F_{r'r'}$ to have their ab initio ratio with respect

to $F_{r'\theta}$. The results are presented in Table VI. The fitted harmonic frequencies presented in Table IV are based on the latter.

As can be seen, both approaches give very similar force constants, with the ratio-constraining set matching almost perfectly with the ab initio results. Compared with Tobiason’s previous result [1], one of the most obvious and easily understandable changes is the increase in F_{rr} , as the harmonic frequency of the CH asymmetric stretching mode of C12 used in this work is significantly larger. A similar argument applies to the torsional force constant. Using our harmonic force constants, both the harmonic frequencies and fundamentals can be predicted for all six vibrational modes of all isotopologues (see Table IV). It is not surprising that the predicted frequencies of fundamentals of mode 1 and 2 of C_2D_2 are rather far away from the values claimed in ref [14], which were used in Tobiason’s analysis [1].

TABLE VI: Force constants of the *trans* conformer of S_1 acetylene. Numbers in asterisks are either constrained to have their ab initio ratio with respect to $F_{r'\theta}$ or constrained to be zero.

a			ab-initio	Tobiason
F_{rr}	5.07(1)	5.06(0)	5.08	4.78(3)
F_{rR}	0.089(18)*	0*	0.086	0*
$F_{rr'}$	0.042(8)*	0.029(6)	0.041	0.138(25)
$F_{r\theta}$	0.216(47)	0.185(43)	0.212	0.188(40)
$F_{r'\theta}$	0.032(6)	0*	0.031	0*
F_{RR}	7.71(2)	7.74(2)	7.75	7.63(2)
$F_{R\theta}$	0.434(50)	0.434(49)	0.417	0.583(21)
$F_{\theta\theta}$	0.545(6)	0.543(6)	0.536	0.541(4)
$F_{\theta\theta'}$	0.114(6)	0.112(6)	0.128	0.127(4)
$F_{\tau\tau}$	0.145(1)	0.145(1)	0.136	0.137(4)

^aUnits are: mdyne/Å for force constants between two bonds (e.g. F_{rr}); mdyne×Å for ones between two angles; and mdyne for ones between a bond and an angle.

V. CONCLUSION

As mentioned earlier in the Introduction, a large portion of this work is made possible after an almost complete characterization of the vibrational structure of the *trans* conformer of S₁ C12 acetylene, in addition to works from relatively fewer but important isotopologue studies of the molecule, including the first part of this work. Specifically, we have determined the rotational and vibrational structure of six Franck-Condon bright states of doubly-substituted carbon-13 acetylene. An updated geometry of the *trans* conformer of S₁ acetylene is then provided. By including both the diagonal and off-diagonal x_{ij} anharmonicities, we obtain harmonic frequencies of four isotopologues of S₁ acetylene, which agree well with ab initio calculations. **GF** matrix method is then applied to obtain harmonic force constants of the molecule, which also agree well with the calculations. This updated set of harmonic force constants, which are believed to be more reliable than Tobiason's previous results, will be used together with our new molecular geometry to refine the S₁-S₀ Franck-Condon calculation.

ASSOCIATED CONTENT

Supporting Information

The rotational line assignments of the six vibrational state of S₁ C13 acetylene reported in this work are presented here. We also provide the **B** matrix, from which the **G** matrices can be determined for all four isotopologues. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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