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# The experimental equilibrium structure of acetylene

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The empirical equilibrium structure of acetylene has been derived by exploiting the very precise experimental rotational constants available in the literature for the 10 isotopologues relative to all the possible combinations of H, D,  $^{12}\text{C}$  and  $^{13}\text{C}$  atoms. The geometry obtained when data for all species are fitted together is:  $r_e(\text{CH}) = 106.167(14)$  pm and  $r_e(\text{CC}) = 120.2866(72)$  pm. This determination shows some systematic residuals due to the singly D-substituted isotopologues. If we exclude such species from the fit, we obtain our most precise evaluation:  $r_e(\text{CH}) = 106.1689(23)$  pm and  $r_e(\text{CC}) = 120.2817(12)$  pm. The possibility of a breakdown of the Born–Oppenheimer approximation has also been tested.

## 1 Introduction

High-resolution spectroscopy provides very accurate information that can be exploited to derive the structures of molecules in the gas phase. Such structures, which describe a geometry calculated at the minimum of the potential energy surface in a hypothetical vibrationless state, are independent of the nuclear masses, within the Born–Oppenheimer (BO) approximation. They are generally difficult to derive from experiments because, for polyatomic molecules, a great deal of spectroscopic data about the parent species and its isotopologues is required. Even when their spectra are accessible and analyzable, the derivation of the molecular spectroscopic parameters can be complicated by the presence of vibrational and ro-vibrational resonances which, if not treated correctly, reduce the accuracy of the experimentally derived constants.

High-level *ab initio* calculations have played a major role in structure determinations and a number of purely theoretical and semi-experimental structures, where empirical constants are corrected by computed parameters, have been published (see the next section for references).

Acetylene is a very basic organic molecule, the simplest containing triple bonds, and is of crucial importance in several fields of chemistry, physical chemistry<sup>1</sup> and combustion.<sup>2</sup> It is also a key species in molecular astrophysics.<sup>3,4</sup> Because of its simplicity, it is a very good test molecule for theoretical calculations and for the derivation of its equilibrium geometry. It is linear and has only two structural parameters,  $r_e(\text{CC})$  and  $r_e(\text{CH})$ . Considering  $^{13}\text{C}$  and D substitutions, 10 isotopologues, and therefore 10 experimental equilibrium rotational constants, can be obtained.

A number of high-resolution infrared and microwave studies have been published on this species in recent years (see for example ref. 5). Very precise spectroscopic parameters were obtained and the rotational constants of the ground and the excited vibrational states of all 10 stable isotopologues of  $\text{C}_2\text{H}_2$  are now available at a very high level of accuracy. All these data can be exploited to obtain an improved, purely empirical equilibrium structure of acetylene. After a careful review of the experimental data available in the literature, several test fits have been performed and discussed. The results are examined to evaluate if the breakdown of a Born–Oppenheimer approximation may occur in acetylene.

## 2 Analysis

### 2.1 Theoretical background and previous work

The calculation of the empirical equilibrium structure of a molecule requires a number of experimental constants. The rotational parameter  $B_v$  can be expressed in terms of the vibration–rotation coupling constants  $\alpha_i$  and  $\gamma_{ij}$  according to

$$B_v = B_c - \sum_i^5 \alpha_i (v_i + d_i/2) + \sum_i^5 \sum_{j \geq i}^5 \gamma_{ij} (v_i + d_i/2)(v_j + d_j/2), \quad (1)$$

where  $d_i$  is 1 for non-degenerate and 2 for doubly-degenerate vibrational modes. Using eqn (1) the equilibrium rotational constant can be calculated as

$$B_c = B_0 + \frac{1}{2} \sum_i^5 \alpha_i d_i - \frac{1}{4} \sum_i^5 \sum_{j \geq i}^5 \gamma_{ij} d_i d_j \quad (2)$$

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In the case of acetylene, the geometry at equilibrium can be derived from the experimental  $B_e$ 's, which are inversely proportional to the principal moment of inertia  $I_e$  at the equilibrium geometry. These are calculated from the highly precise rotational constants in the ground state  $B_0$  and the values of the five  $\alpha_i$ 's for each isotopologue, neglecting the higher-order terms  $\gamma_{ij}$  in eqn (2). Their contribution will be discussed later. Several papers have been published in which the equilibrium geometry of acetylene has been derived according to this procedure. Below, only the most recent and meaningful contributions are described.

In 2002, Pawlowski *et al.*<sup>6</sup> applied the experimental/theoretical approach described by Pulay<sup>7</sup> to the calculation of the equilibrium structures of many molecules, including  $C_2H_2$ , within the Born–Oppenheimer approximation.

The experimental ground state rotational constants of many isotopologues were corrected by the sums over the vibrational modes (see eqn (1)) of the computed *ab initio*  $\alpha_i$ . The significant advantage is that the sum of the  $\alpha_i$ 's is free from Coriolis resonance terms. In fact, the Coriolis resonance contributions cancel each other and this is true for both theoretical and experimental sums. Also, the expression of the  $\alpha_i$ 's does not contain Fermi resonance terms. Experimentally determined constants can, on the other hand, be affected by Fermi resonances. The most accurate  $\sum_i \alpha_i$  for 5 isotopologues of acetylene, calculated at the CCSD(T)/cc-pVQZ level, were used to determine the semi-experimental equilibrium bond lengths,  $r_e(CC) = 120.356(57)$  pm and  $r_e(CH) = 106.166(50)$  pm.

Heckert *et al.*<sup>8</sup> calculated a purely theoretical equilibrium geometry, showing that the basis set extrapolation technique (BSE) could be used in conjunction with coupled cluster theory in geometry optimizations. The calculated equilibrium structure was  $r_e(CC) = 120.304$  pm and  $r_e(CH) = 106.166$  pm.

Cazzoli *et al.*<sup>9</sup> recorded pure rotational transitions for DCCH,  $D^{13}CCH$  and  $DC^{13}CH$  and a semi-experimental equilibrium structure was derived using ground state rotational constants for ten isotopologues. The  $\sum_i \alpha_i$  were calculated at the CCSD(T)/cc-pwCVQZ level, higher than that adopted in ref. 6. Hence, improved values of the equilibrium geometry were obtained,  $r_e(CC) = 120.289(1)$  pm and  $r_e(CH) = 106.176(2)$  pm.

In 2011, Liévin *et al.*<sup>10</sup> determined the most accurate equilibrium structure of acetylene so far. They derived three types of equilibrium geometries: *ab initio*, semi-experimental and experimental. The *ab initio* calculations tested the contribution of relativistic effects, inner shell correlation, diffuse functions and diagonal Born–Oppenheimer corrections. The semi-experimental structure was determined following the procedure of ref. 9, combining the  $B_0$  of ten isotopologues with the  $\sum_i \alpha_i$  computed at a CCSD(T)/wCVQZ level. As for the experimental structure, empirical values of  $B_0$  and  $\sum_i \alpha_i$  of the five species  $H^{12}C^{12}CH$ ,  $H^{12}C^{13}CH$ ,  $H^{13}C^{13}CH$ ,  $D^{12}C^{12}CH$  and  $D^{12}C^{12}CD$  were used. The authors highlighted a systematic deviation in the semi-experimental fit performed on ten isotopologues. The contribution of the  $\gamma_{ij}$  constants was not considered in the expansion of

$B_0$  because it was estimated to be about 400 kHz, too small to give a sizable contribution and to eliminate the residual correlation. Moreover, the importance of the BO breakdown was investigated by allowing the CH and CD bond distances to be fitted simultaneously. The variation of these bond lengths appeared too big, if compared to the estimated diagonal Born–Oppenheimer corrections (DBOC), and the correlation still persisted. In conclusion, the systematic deviation found in the semi-experimental fit remained unexplained. Also, the derivation of the equilibrium structure from purely empiric constants was not free from irregularities. The CC and CH bond distances were fully correlated and anomalous deviations arose for  $H^{12}C^{12}CH$  and  $H^{12}C^{13}CH$ .

## 2.2 Spectroscopic parameters used for the analysis

The choice of the experimental spectroscopic parameters of acetylene and its isotopologues, among all those present in literature, was made on the basis of their precision and homogeneity. For some isotopic species, very large global fits, including high energy vibrational states, are available in the literature. However, the parameters obtained often are not comparable to those determined using restricted sets of data and are less precise. Indeed, the accuracy of the constants achieved through the introduction of rather extended Hamiltonians is sometimes reduced by the inevitable correlation among the fitted parameters and by the effects of perturbations, which increase in number and magnitude as the energy increases. So, we generally preferred data from more limited analyses, usually considering only the fundamentals and their first overtones and combination bands which mostly provide a better precision and high homogeneity among the parameters of different isotopic species. Only in the case of  $^{12}C_2D_2$  and  $^{12}C^{13}CD_2$  did all the required constants come from one single study for each molecule, while for the other isotopologues they were taken from several papers. An additional source of dissimilarity is that the very precise data derived from pure rotational spectroscopy are available only for the molecules of  $C_{\infty v}$  symmetry. The  $B_0$ ,  $\alpha_i^0$  and  $\gamma_{ij}^0$  constants for all isotopologues are collected in Tables 1 and 2.

A global fit of the vibrational states up to  $8600\text{ cm}^{-1}$  was performed by Amyay *et al.*<sup>11</sup> for  $H^{12}C^{12}CH$  and by Robert *et al.*<sup>12</sup> for  $H^{12}C^{13}CH$  resulting in complete sets of  $B_0$ ,  $\alpha_i^0$  and  $\gamma_{ij}^0$ . However, the parameter values obtained are less precise than those we used. Similar conclusions can be drawn for the parameters of the global fit for  $H^{13}C^{13}CH$ .<sup>13</sup>

## 3 Results and discussion

### 3.1 Results

The first part of the analysis was performed by deriving the values of  $B_e$  from eqn (2) using the data in Table 1 and neglecting the contributions of  $\gamma_{ij}$ . These values are listed in Table 3. The error of  $B_e$ , that ranges from  $189 \times 10^{-9}$  to  $680 \times 10^{-9}\text{ cm}^{-1}$ , has been calculated from the statistical propagation of the  $B_0$  and  $\alpha_i^0$  uncertainties. As expected, the errors of  $B_e$  are larger than those of  $B_0$  since they reflect the  $\alpha_i^0$  statistical errors.

**Table 1** Experimental values (in cm<sup>-1</sup>) of the rotational constants  $B_0$  and vibration rotation interaction constants  $\alpha_i^0$  of acetylene and its isotopologues<sup>a</sup>

Parameter	<sup>12</sup> CH <sup>12</sup> CH	Ref.	<sup>12</sup> CH <sup>13</sup> CH	Ref.	<sup>13</sup> CH <sup>13</sup> CH	Ref.	<sup>12</sup> CD <sup>12</sup> CD	Ref.	<sup>12</sup> CD <sup>13</sup> CD	Ref.
$B_0$	1.1766461800(100)	23	1.148460772(435)	27	1.119574352(174)	29	0.8478734706(168)	32	0.833118683(474)	33
$\alpha_1^0 \times 10^3$	6.843000(69)	24	6.513611(617)	28	6.124486(638)	30	5.981994(285)	32	5.722665(324)	33
$\alpha_2^0 \times 10^3$	6.180580(21)	23	5.983216(427)	28	5.808371(170)	30	3.162298(170)	32	3.109181(366)	33
$\alpha_3^0 \times 10^3$	5.881760(89) <sup>b</sup>	25	5.573690(525)	28	5.311898(512) <sup>b</sup>	31	4.491143(178)	32	4.316416(387)	33
$\alpha_4^0 \times 10^3$	-1.3535350(860)	26	-1.187191(161)	27	-1.031341(141)	29	-2.08049802(902)	32	-1.946066(209)	33
$\alpha_5^0 \times 10^3$	-2.2320750(400)	26	-2.082555(193)	27	-1.9303064(945)	29	-2.16654528(895)	32	-2.075198(103)	33
Parameter	<sup>13</sup> CD <sup>13</sup> CD	Ref.	<sup>12</sup> CH <sup>12</sup> CD	Ref.	<sup>12</sup> CH <sup>13</sup> CD	Ref.	<sup>12</sup> CD <sup>13</sup> CH	Ref.	<sup>13</sup> CH <sup>13</sup> CD	Ref.
$B_0$	0.817872207(450)	34	0.99152746042(798)	38	0.9752708273(562)	40	0.9671933960(484)	40	0.9503316739(136)	42
$\alpha_1^0 \times 10^3$	5.383201(702)	35	4.859699(178)	39	4.765284(350) <sup>b</sup>	41	4.487067(412) <sup>b</sup>	41	4.389164(472)	43
$\alpha_2^0 \times 10^3$	3.058969(227)	36	4.293623(474)	39	4.229106(368) <sup>b</sup>	41	4.173194(356) <sup>b</sup>	41	4.097933(185)	43
$\alpha_3^0 \times 10^3$	4.161986(164)	37	6.699267(192)	39	6.295277(295) <sup>b</sup>	41	6.530547(235) <sup>b</sup>	41	6.090601(402)	43
$\alpha_4^0 \times 10^3$	-1.834228(100)	34	-2.6433354(162)	38	-2.409888(172)	40	-2.538037(147)	40	-2.3033996(292)	42
$\alpha_5^0 \times 10^3$	-1.9594838(788)	34	-1.4813042(109)	38	-1.452763(153)	40	-1.322326(135)	40	-1.2837290(264)	42

<sup>a</sup> Estimated uncertainties (1 $\sigma$ ) are given in parentheses in units of the last figure quoted. <sup>b</sup> The  $\alpha_i$  value has been calculated as  $B_0 - B_{v_i}$ .

It must be emphasized that for most isotopologues the vibration-rotation constants have been obtained from fitting procedures including the appropriate  $l$ -type vibration and anharmonic resonance terms affecting the band systems analyzed. Thus, these values do not contain those perturbation effects.

From the 10 values of the moment of inertia at equilibrium  $I_e$ , the  $r_e(\text{CC})$  and  $r_e(\text{CH})$  bond lengths were calculated by means of a least squares fit. For a general linear molecule with an arbitrary number of masses,  $I$  can be expressed by the equation:

$$I = \frac{\frac{1}{2} \sum_j \sum_i m_i m_j r_{ij}^2}{\sum_i m_i} \quad (3)$$

where  $r_{ij}$  is the distance between masses  $m_i$  and  $m_j$ .<sup>14</sup> The weight attributed to each  $I_e$  is the inverse of the squared uncertainty of the moment of inertia.

It must be pointed out that the vibration-rotation interaction constants  $\alpha_i^0$  and  $\gamma_{ij}^0$  were obtained from the analysis of the experimental data according to the equation<sup>15,16</sup>

$$\begin{aligned}
 F(v, l, J) = & \left[ B_0 - \sum_i \alpha_i^0 v_i + \sum_{i \leq j} \gamma_{ij}^0 v_i v_j + \sum_{b \leq b' = 4,5} \gamma^{b'b'} l_b l_{b'} \right. \\
 & \left. + \sum_{i \leq j \leq m} \varepsilon_{ijm} v_i v_j v_m + \sum_{i, b \leq b' = 4,5} \varepsilon_i^{b'b'} v_i l_b l_{b'} \right] [M - k^2] \\
 & - \left[ D_0 + \sum_i \beta_i^0 v_i + \sum_{i \leq j} \delta_{ij}^0 v_i v_j + \sum_{b \leq b'} \delta^{b'b'} l_b l_{b'} \right. \\
 & \left. + \sum_{i \leq j \leq m} \theta_{ijm} v_i v_j v_m + \sum_{i, b \leq b' = 4,5} \theta_i^{b'b'} v_i l_b l_{b'} \right] [M - k^2] \\
 & + \left[ H_0 + \sum_i h_i v_i \right] [M - k^2]
 \end{aligned} \quad (4)$$

with  $M = J(J + 1)$ ,  $k = l_4 + l_5$ , and  $l_4, l_5$  the vibrational angular momentum quantum numbers of the bending modes.

Unlike  $\alpha_i$  in eqn (1) and (2), the  $\alpha_i^0$  values include the contribution of the higher order terms  $\gamma_{ij}$  according to

$$\alpha_i^0 = \alpha_i - \gamma_{ii} d_i - \frac{1}{2} \sum_{j \neq i} \gamma_{ij} d_j \quad (5)$$

and the  $\gamma_{ij}^0$  values include, in principle, the contribution of higher order  $\varepsilon_{ij}$ -type terms. However, we assumed that  $\gamma_{ij}^0 = \gamma_{ij}$ , neglecting the effects of  $\varepsilon_{ijk}$ , that generally are set to zero in the fitting procedures.

For our derivations we used atomic masses instead of nuclear masses, consistent with the calculations reported in the literature. These values are: 1.007825032231(93) u, 2.014101778120(122) u and 13.003354835071(227) u, for H, D and <sup>13</sup>C respectively.<sup>17</sup> The quoted errors of the masses have not been considered in the evaluations of the uncertainties of  $r_e(\text{CC})$  and  $r_e(\text{CH})$  because they are negligible with respect to the errors of  $I_e$ .

The results of the fits are reported in Table 4. The derived distances obtained with 10 isotopologues (fit 9 of Table 4) are comparable to those of Liévin *et al.*<sup>10</sup> but less precise. A possible explanation could be that in ref. 10 they used only five values of  $B_e$  with uncertainties which strongly reduce the contribution of the deuterated species in the least squares fit. The standard deviation of the fit is 8.21  $\mu\text{m}^2$ . The  $r_e(\text{CC})$  and  $r_e(\text{CH})$  distances are less correlated than those in ref. 10: 98% instead of 100%. A smaller correlation was, indeed, expected fitting ten values of  $I_e$  with similar weights, ranging from  $0.4 \times 10^2$  to  $0.5 \times 10^3 \text{ u}^{-2} \text{ pm}^{-4}$ . Moreover, the difference between observed and calculated values of  $I_e$  was positive for the four isotopologues containing both H and D and negative for the others. This systematic distribution of the residuals highlights that the analyzed data set could contain incongruent elements or that there are intrinsic inconsistencies. The same systematic deviation was observed also by Liévin *et al.*<sup>10</sup> in the calculation of the semi-experimental geometry.

**Table 2** Experimental values in  $\text{cm}^{-1}$  of the vibration–rotation interaction constants  $\gamma_{ij}^0$  of acetylene and its isotopologues. For  $^{12}\text{CH}^{12}\text{CH}$  and  $^{12}\text{CH}^{13}\text{CH}$  the constants from the global fit are also reported<sup>a</sup>

Parameter	$^{12}\text{CH}^{12}\text{CH}$	Ref.	$^{12}\text{CH}^{12}\text{CH}$	Ref.	$^{12}\text{CH}^{13}\text{CH}$	Ref.	$^{12}\text{CH}^{13}\text{CH}$	Ref.
$\gamma_{11} \times 10^5$			−6.81(49)	11			−10.23(33)	12
$\gamma_{12} \times 10^5$			6.914(69)	11			5.812(45)	12
$\gamma_{13} \times 10^5$			−1.772(40)	11			−19.66(54)	12
$\gamma_{14} \times 10^5$			1.159(42)	11			8.95(11)	12
$\gamma_{15} \times 10^5$			3.754(66)	11			2.886(24)	12
$\gamma_{22} \times 10^5$			−1.035(40)	11	−1.3360(24)	28	−2.139(32)	12
$\gamma_{23} \times 10^5$			7.084(73)	11			6.362(79)	12
$\gamma_{24} \times 10^5$	−7.238(33)	23	−7.569(43)	11	−6.901(33)	28	−6.784(36)	12
$\gamma_{25} \times 10^5$	−5.814(34)	23	−5.552(18)	11	−5.374(38)	28	−5.301(18)	12
$\gamma_{33} \times 10^5$			2.21(51)	11			7.07(33)	12
$\gamma_{34} \times 10^5$			4.710(34)	11			6.264(98)	12
$\gamma_{35} \times 10^5$			2.550(37)	11			2.664(48)	12
$\gamma_{44} \times 10^5$	0.0900(48)	26	−0.4335(62)	11	0.2001(48)	27	−0.3901(13)	12
$\gamma_{45} \times 10^5$	−2.3716(20)	26	−2.185(12)	11	5.190(53)	27	−2.105(93)	12
$\gamma_{55} \times 10^5$	1.8699(19)	26	2.4383(62)	11	1.885(10)	27	2.2985(42)	12
$\sum_{ij} \gamma_{ij} \frac{d_i d_j}{4} \times 10^5$	−6.938(24)		0.99(19)		0.803(60)		0.95(17)	
Parameters	$^{13}\text{CH}^{13}\text{CH}$	Ref.	$^{12}\text{CD}^{12}\text{CD}$	Ref.	$^{12}\text{CD}^{13}\text{CD}$	Ref.	$^{13}\text{CD}^{13}\text{CD}$	Ref.
$\gamma_{11} \times 10^5$			8.208(23)	32	7.053(26)	33		
$\gamma_{12} \times 10^5$					15.11(37)	33		
$\gamma_{13} \times 10^5$			−7.620(23)	32	−13.976(42)	33		
$\gamma_{14} \times 10^5$			11.095(19)	32	11.000(21)	33		
$\gamma_{15} \times 10^5$			−0.579(11)	32	0.598(20)	33		
$\gamma_{22} \times 10^5$			−0.362(13)	32	−0.226(23)	33		
$\gamma_{23} \times 10^5$			8.520(23)	32	7.8014(77)	33		
$\gamma_{24} \times 10^5$	−5.602(28)	30	−9.233(76)	32	−7.239(79)	33	−5.807(14)	36
$\gamma_{25} \times 10^5$	−4.962(15)	30	−6.244(15)	32	−6.318(62)	33	−7.05(17)	36
$\gamma_{33} \times 10^5$			−9.28(14)	32	−0.591(45)	33		
$\gamma_{34} \times 10^5$			2.5660(65)	32	2.512(11)	33	2.3113(78)	37
$\gamma_{35} \times 10^5$			5.130(16)	32	4.3036(95)	33	3.733(16)	37
$\gamma_{44} \times 10^5$	0.2982(46)	29	−1.92991(81)	32	−1.2771(74)	33	−1.036(21)	34
$\gamma_{45} \times 10^5$	4.289(48)	29	−0.1908(30)	32	−0.154(13)	33	−0.3240(64)	34
$\gamma_{55} \times 10^5$	1.7782(46)	29	1.95915(84)	32	9.2462(38)	33	1.181(20)	34
$\sum_{ij} \gamma_{ij} \frac{d_i d_j}{4} \times 10^5$	1.083(51)		3.161(43)		14.04(11)		−3.583(91)	
Parameters	$^{12}\text{CH}^{12}\text{CD}$	Ref.	$^{12}\text{CH}^{13}\text{CD}$	Ref.	$^{12}\text{CD}^{13}\text{CH}$	Ref.	$^{13}\text{CH}^{13}\text{CD}$	Ref.
$\gamma_{11} \times 10^5$			−2.684(49)	42	−24.247(72)	42	−0.634(32)	43
$\gamma_{12} \times 10^5$							1.777(73)	43
$\gamma_{13} \times 10^5$							−1.890(83)	43
$\gamma_{14} \times 10^5$	−2.683(31)	39					−77.07(15)	43
$\gamma_{15} \times 10^5$	13.330(51)	39					−0.3269(85)	43
$\gamma_{22} \times 10^5$	−0.504(19)	39					6.209(63)	43
$\gamma_{23} \times 10^5$							−10.998(15)	43
$\gamma_{24} \times 10^5$	−12.868(27)	39					−1.8370(81)	43
$\gamma_{25} \times 10^5$	−8.739(87)	39					−3.564(33)	43
$\gamma_{33} \times 10^5$			6.21(15)	41	−2.261(63)	41	−3.564(33)	43
$\gamma_{34} \times 10^5$	16.507(45)	39	36.2(11)	41	15.70(18)	41	13.209(37)	43
$\gamma_{35} \times 10^5$	−4.173(47)	39	−3.65(10)	41	−4.514(75)	41	−5.231(55)	43
$\gamma_{44} \times 10^5$	3.20827(11)	38	2.7660(78)	40	3.15131(64)	40	3.0314(21)	42
$\gamma_{45} \times 10^5$	−2.54007(77)	38	−2.41946(77)	40	−2.78384(69)	40	−2.4141(61)	42
$\gamma_{55} \times 10^5$	2.386750(33)	38	2.09485(58)	40	2.08408(50)	40	2.2348(20)	42
$\sum_{ij} \gamma_{ij} \frac{d_i d_j}{4} \times 10^5$	3.616(64)		19.60(55)		1.42(10)		−38.192(98)	

<sup>a</sup> Estimated uncertainties ( $1\sigma$ ) are given in parentheses in units of the last figure quoted.

To verify if a contribution had not been accounted for properly in the structure calculation we evaluated first the influence of the higher order vibration rotation interaction constants  $\gamma_{ij}$  in the determination of  $B_e$ . These experimental parameters were collected from the literature, as specified in Section 2.2, and new values of  $B_e$  were obtained. However, taking into account the  $\gamma_{ij}$  constants presents severe problems.

The number of known constants is not homogeneous for the 10 isotopologues and the values of the same constants obtained from different literature sources may differ in sign and/or order of magnitude, depending on the complexity of the data analysis, as in the case of  $^{12}\text{C}_2\text{H}_2$  and  $^{12}\text{CH}^{13}\text{CH}$  (see Table 2). Moreover, since the values of  $\gamma_{ij}$  are generally two orders of magnitude smaller than those of  $\alpha_i$ , and have uncertainties of

Table 3 Ground state, equilibrium rotational constants and equilibrium moments of inertia of acetylene and its isotopologues

Isotopologue	$B_0/\text{cm}^{-1}$	$\sigma/10^{-9} \text{ cm}^{-1}$	$B_e/\text{cm}^{-1}$	$\sigma/10^{-9} \text{ cm}^{-1}$	$I_e^a/\text{u pm}^2$
$^{12}\text{CH}^{12}\text{CH}$	1.1766461800	10.0	1.182513240	581	142557.64(7)
$^{12}\text{CH}^{13}\text{CH}$	1.148460772	435	1.154226284	680	146051.34(9)
$^{13}\text{CH}^{13}\text{CH}$	1.119574352	174	1.125235082	483	149814.29(7)
$^{12}\text{CD}^{12}\text{CD}$	0.8478734706	16.8	0.850444145	189	198221.47(5)
$^{12}\text{CD}^{13}\text{CD}$	0.833118683	474	0.835671550	613	201725.54(15)
$^{13}\text{CD}^{13}\text{CD}$	0.817872207	450	0.820380573	606	205485.47(15)
$^{12}\text{CH}^{12}\text{CD}$	0.99152746042	7.98	0.995329115	272	169367.39(5)
$^{12}\text{CH}^{13}\text{CD}$	0.9752708273	56.2	0.979053011	377	172183.01(7)
$^{12}\text{CD}^{13}\text{CH}$	0.9671933960	48.4	0.970928437	361	173623.81(7)
$^{13}\text{CH}^{13}\text{CD}$	0.9503316739	13.6	0.954033394	326	176698.52(6)

<sup>a</sup> Estimated uncertainties ( $1\sigma$ ) are given in parentheses in units of the last figure quoted.

the same order of magnitude, the calculated  $B_e$  values are affected by larger errors. We also considered obtaining  $B_e$  of all the isotopologues by subtracting from  $B_0$  the value of  $(1/4) \sum_i \sum_{j \geq i} \gamma_{ij} d_i d_j$  calculated for  $^{12}\text{C}_2\text{H}_2$ .

However, this treatment of the data is arbitrary since that sum is characteristic of each isotopologue being about  $0.99 \times 10^{-5} \text{ cm}^{-1}$  for  $^{12}\text{C}_2\text{H}_2$ ,  $0.95 \times 10^{-5} \text{ cm}^{-1}$  for  $^{12}\text{C}^{13}\text{CH}_2$ ,  $14.0 \times 10^{-5} \text{ cm}^{-1}$  for  $^{12}\text{C}^{13}\text{CD}_2$ ,  $3.2 \times 10^{-5} \text{ cm}^{-1}$  for  $^{12}\text{C}_2\text{D}_2$  and  $-38.2 \times 10^{-5} \text{ cm}^{-1}$  for  $^{13}\text{C}_2\text{HD}$  (see Table 2). Lastly, the use of  $\alpha_i^0$  instead of  $\alpha_i$  in eqn (2) truncated as  $B_e = B_0 + \frac{1}{2} \sum_i \alpha_i^0 d_i$  somehow includes implicitly the contribution of  $\gamma_{ij}$  on  $B_e$ , as can be easily verified by substitution of eqn (5) in the former expression. For all these reasons the  $\gamma_{ij}$  constants were not included explicitly in the calculation of  $B_e$  assuming that this approximation is not responsible for the trends of the residuals of the fit and of the high correlation between  $r_e(\text{CC})$  and  $r_e(\text{CH})$  in fit 9. To clarify these points we made several fits using different subgroups of  $I_e$ , formed by at least three data sets. The criteria adopted to group the isotopologues were the isotopes bonded to the carbons and the symmetry of the molecules. The results are reported in Table 4 and will be compared with those of fit 9 taken as reference.

Four different groups of three isotopologues were formed, one containing only hydrogen atoms bonded to the carbons (set1), one with only deuterium (set2) and the others with both H and D (set3 and set4). The resulting standard deviation of the fits is smaller than that of fit 9, whereas the statistical errors of the bond lengths are smaller only for set1 and set3. This is due to the relative weights of the fitted  $I_e$  values in each subgroup. The length values change abruptly from set1 to set2, set3 and set4 following what was expected from isotopic substitution. The  $r_e(\text{CH})$  value is longer in set1 (H atoms) than in set2 (D atoms), while in set3 and set4 (H and D atoms) it almost corresponds to the mean of the former values. The same trend is observed if we consider the sum of the CH and CC bonds, 226.472(3) pm, 226.43(3) pm and 226.45(2) pm in fits 1, 2 and 3/4. Since the two structural parameters are 100% correlated, two additional fits were performed, keeping  $r_e(\text{CC})$  fixed to the mean value 120.29 pm while refining  $r_e(\text{CH})$  (see fits 1a and 2a in Table 4). This value changed by about 0.05 pm becoming more similar to that resulting from set3 and set4 and to the reference fit.

Set5 and set6 comprise four molecules: all the isotopologues containing both H and D atoms (set5), and those of  $D_{\infty h}$  symmetry (set6). As expected, the results of set5 are almost midway between those of set3 and set4, as far as the standard deviation of the fit and the precision of the structure are concerned. However, the bond length correlation is still 100%. On the other hand, the  $r_e(\text{CC})$  and  $r_e(\text{CH})$  values from set6 are more precise than the previous ones and less correlated: 97% instead of 100%. Next, two further tests were performed: one adding  $^{12}\text{C}^{13}\text{CH}_2$  and  $^{12}\text{C}^{13}\text{CD}_2$  to the molecules of set6 (set7) and one grouping all the  $C_{\infty v}$  isotopologues (set8). Fit 7 confirms the results of fit 6 with better standard deviation and precision while fit 8 is affected by a poor standard deviation, low precision and 100% correlation between the two bond lengths. The  $r_e(\text{CC})$  and  $r_e(\text{CH})$  values obtained in fit 7 and fit 8 overlap within  $2\sigma$  and  $r_e(\text{CH})$  in fit 8 lengthens to 106.188 pm at the expense of  $r_e(\text{CC})$ .

Among the listed results, the more precise and less correlated values of equilibrium geometry are those from fit 7. They overlap within  $1\sigma$  with those from the complete set of  $I_e$ . The distribution of residuals in the various tests is specified in the last column of Table 4 and does not show systematic trends, except in fits 8 and 9.

The fits described so far converge to slightly different bond lengths. Since the performed fits employ sets of data relative to different isotopic substitutions, we considered it appropriate to verify if any evidence of the breakdown of the BO approximation could be deduced. The equilibrium geometry was therefore obtained refining three parameters in the subgroups with at least four members and not all center symmetric, fits 5b, 7b, 8b and 9b in Table 4. Only the results of fits 8b and 9b are truly meaningful since the structural parameters are much less correlated than in previous fits. The standard deviations of the fits are comparable and smaller than in fit 9. In both fits one CH distance is longer and one shorter than the values in fits 8 and 9, whereas the CC distances are practically identical. The structural parameters overlap within  $1\sigma$  and in both cases have precisions close to those of fits 8 and 9. The mean values of the  $r_e(\text{CH})$  of bond 1 and bond 2 are consistent with the corresponding value of  $r_e(\text{CH})$  in fit 8 and in fit 9, respectively, and overlap each other within  $1\sigma$ . The sign of the residuals does not change in fits 8b and 9b with respect to fits 8 and 9. From these results, a decisive indication of the breakdown of the BO

Table 4 Equilibrium structural parameters of acetylene from several fits using different sets of isotopologues<sup>a</sup>

Fit no	Isotopologue	$r_c(\text{CH})$ bond 1/pm	$r_c(\text{CC})/\text{pm}$	$r_c(\text{CH})$ bond 2/pm	Fit standard deviation/ $\mu\text{ pm}^2$	Correlation <sup>b</sup> %	Sign of residual
1 1a	<sup>12</sup> CH <sup>12</sup> CH	106.2024(25)	120.26955(92)		0.08	100	–
	<sup>13</sup> CH <sup>13</sup> CH	106.1462(11)	120.29 <sup>c</sup>		1.32		–
	<sup>12</sup> CH <sup>13</sup> CH						+
2 2a	<sup>12</sup> CD <sup>12</sup> CD	106.103(28)	120.323(18)		1.11	100	+
	<sup>13</sup> CD <sup>13</sup> CD	106.15571(72)	120.29 <sup>c</sup>		1.67		+
	<sup>12</sup> CD <sup>13</sup> CD						–
3	<sup>12</sup> CH <sup>12</sup> CD	106.1620(92)	120.2926(46)		0.4	100	+
	<sup>13</sup> CH <sup>13</sup> CD						+
	<sup>12</sup> CH <sup>13</sup> CD						–
4	<sup>12</sup> CH <sup>12</sup> CD	106.163(21)	120.292(10)		0.91	100	+
	<sup>13</sup> CH <sup>13</sup> CD						+
	<sup>13</sup> CH <sup>12</sup> CD						–
5 5b	<sup>12</sup> CH <sup>12</sup> CD	106.163(15)	120.2919(75)		0.68	100 99; 98; 100	++
	<sup>13</sup> CH <sup>13</sup> CD	106.1597(90)	120.2926(44)	106.1633(88)	0.44		++
	<sup>12</sup> CH <sup>13</sup> CD						--
	<sup>13</sup> CH <sup>12</sup> CD						--
6	<sup>12</sup> CH <sup>12</sup> CH	106.1690(36)	120.2817(19)		1.89	97	+
	<sup>13</sup> CH <sup>13</sup> CH						–
	<sup>12</sup> CD <sup>12</sup> CD						–
	<sup>13</sup> CD <sup>13</sup> CD						+
7 7b	<sup>12</sup> CH <sup>12</sup> CH	106.1689(23)	120.2817(12)		1.49	97 20; 100; 23	++
	<sup>13</sup> CH <sup>13</sup> CH	106.16(16)	120.2817(14)	106.17(16)	1.73		--
	<sup>12</sup> CD <sup>12</sup> CD						--
	<sup>13</sup> CD <sup>13</sup> CD						++
	<sup>12</sup> CH <sup>13</sup> CH						++
	<sup>12</sup> CD <sup>13</sup> CD						--
8 8b	<sup>12</sup> CH <sup>12</sup> CD	106.188(24)	120.279(12)		5.64	100 91; 72; 94	++
	<sup>13</sup> CH <sup>13</sup> CD	106.180(30)	120.279(13)	106.192(28)	6.23		++
	<sup>12</sup> CH <sup>13</sup> CD						++
	<sup>13</sup> CH <sup>12</sup> CD						++
	<sup>12</sup> CH <sup>13</sup> CH						--
	<sup>12</sup> CD <sup>13</sup> CD						--
9 9b	All	106.167(14)	120.2866(72)		8.21	98 64; 10; 77	See text
		106.149(18)	120.2856(68)	106.185(18)	7.76		

<sup>a</sup> Estimated uncertainties ( $1\sigma$ ) are given in parentheses in units of the last figure quoted. <sup>b</sup> In the cases of three structural parameters, the correlation refers to  $r_c(\text{CH})$  bond 1 with  $r_c(\text{CC})$ ;  $r_c(\text{CH})$  bond 1 with  $r_c(\text{CH})$  bond 2; and  $r_c(\text{CC})$  with  $r_c(\text{CH})$  bond 2, respectively. <sup>c</sup> Constrained value, see text.

Table 5 Equilibrium structural parameters of acetylene from significant fits of this work compared to the results of ref. 10<sup>a</sup>

Parameter	This work fit 7	This work fit 9	This work fit 9b	Ref. 10 exp.	Ref. 10 semiexp.	Ref. 10 <i>ab initio</i>	Ref. 10 <i>ab initio</i> + DBOC
$r_c(\text{CH})$ bond 1/pm	106.1689(23)	106.167(14)	106.149(18)	106.168(8)	106.164(1)	106.149	106.152
$r_c(\text{CC})/\text{pm}$	120.2817(12)	120.2866(72)	120.2856(68)	120.286(3)	120.2958(7)	120.265	120.28
$r_c(\text{CH})$ bond 2/pm			106.185(18)				
no. of isotopologues used in the fit	6	10	10	5	10		
St. dev./ $\mu\text{ pm}^2$	1.49	8.21	7.76				

<sup>a</sup> Estimated uncertainties ( $1\sigma$ ) are given in parentheses in units of the last figure quoted.

## 4 Conclusions

approximation in acetylene cannot be inferred. The most significant structures derived in this work, namely fits 7, 9 and 9b, are collected in Table 5, where the results obtained in ref. 10 are also listed for comparison.

The equilibrium geometry of acetylene has been evaluated entirely from experiment. The rotational constants  $B_e$  used for the calculations have been obtained from the most accurate

experimental values of  $B_0$  and  $\alpha_i^0$  available in the literature for acetylene and its stable isotopologues, *i.e.* for 10 molecular species. Several fits have been performed, with different selections of experimental data pertaining to congruent sets of isotopologues. Large differences between the values of  $r_e(\text{CH})$  and  $r_e(\text{CC})$  bond distances are observed fitting data of sets containing only H or only D isotopes (fits 1 and 2 in Table 4), which, however, overlap within  $3\sigma$ . In all the other fits, which include both H and D isotopically substituted species, values of bond lengths intermediate between the extreme values of fits 1 and 2 were obtained. The only exception is fit 8. The equilibrium geometry obtained when the complete set of experimental data is analyzed is:  $r_e(\text{CH}) = 106.167(14)$  pm and  $r_e(\text{CC}) = 120.2866(72)$  pm. The most precise determination, obtained excluding the singly D-substituted isotopologues, is  $r_e(\text{CH}) = 106.1689(23)$  pm and  $r_e(\text{CC}) = 120.2817(12)$  pm, indistinguishable from the previous one within one standard deviation. Our results are in very good agreement with those calculated applying the semi-experimental approach on the data of 10 isotopologues.<sup>10</sup>

A systematic distribution of the residuals may suggest some effect not accounted for explicitly in our analysis. A possibility is the breakdown of the Born–Oppenheimer approximation, which has been investigated fitting three parameters (two CH bonds and one CC bond). The introduction of an additional structural parameter, however, did not give a clear-cut answer to the question. To date, there are no theoretical expressions that allow the derivation of BO bond lengths and correction parameters for tetraatomic species, analogously to diatomic<sup>18</sup> and linear triatomic<sup>19</sup> molecules. Liévin<sup>10</sup> pointed out that calculated DBOC are unlikely to be responsible for the anomalies of the fit. About this, we recall the results obtained for  $\text{CO}_2$  by Teffo, who showed that in carbon dioxide the nonadiabatic effects exceed the adiabatic ones.<sup>19</sup> He calculated the nonadiabatic parameter for oxygen from which the rotational  $g_f$ -factor  $g_f, -0.052(7)$ , could be determined. Its value is in good agreement with that measured from Zeeman experiments ( $-0.05508(5)$ ).<sup>19</sup> Concerning the CH bond, in the literature are reported the results for the CH radical which, however, differs from acetylene, being an open shell species. Two experimentally derived values are reported for the equilibrium bond length  $r_e$  for CH and CD,  $111.9789(6)$  pm<sup>20</sup> and  $111.8883(5)$  pm,<sup>21</sup> respectively. The large difference between these distances has been attributed to nonadiabatic effects.<sup>22</sup> From these values Martin calculated a BO bond distance  $r_e^{\text{BO}}$  of  $111.774(4)$  pm in excellent agreement with the calculated *ab initio* value.<sup>22</sup>

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