Synthesis, High-Resolution Infrared Spectroscopy, and Vibrational Structure of Cubane, C₈H₈

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ABSTRACT: Carbon-cage molecules have generated a considerable interest from both experimental and theoretical points of view. We recently performed a high-resolution study of adamantane ($C_{10}H_{16}$), the smallest hydrocarbon cage belonging to the diamandoid family (Pirali, O.; et al. *J. Chem. Phys.* **2012**, *136*, 024310). There exist another family of hydrocarbon cages with additional interesting chemical properties: the so-called platonic hydrocarbons that comprise dodecahedrane ($C_{20}H_{20}$) and cubane (C_8H_8). Both possess C–C bond angles that deviate from the tetrahedral angle (109.8°) of the sp³ hybridized form of carbon. This generates a considerable strain in the molecule. We report a new wide-range high-resolution study of the infrared spectrum of cubane. The sample was synthesized in Bari upon decarboxylation of 1,4-cubanedicarboxylic acid thanks to the improved synthesis of literature. Several spectra have been recorded at the AILES beamline of the SOLEIL synchrotron facility. They cover the 600–3200 cm⁻¹ region. Besides



the three infrared-active fundamentals (ν_{10} , ν_{11} , and ν_{12}), we could record many combination bands, all of them displaying a wellresolved octahedral rotational structure. We present here a preliminary analysis of some of the recorded bands, performed thanks the SPVIEW and XTDS software, based on the tensorial formalism developed in the Dijon group. A comparison with ab initio calculations, allowing to identify some combination bands, is also presented.

I. INTRODUCTION

Carbon-cage molecules like fullerenes have generated considerable interest from both experimental and theoretical points of view. Adamantane is the smallest hydrocarbon cage that we could study recently at high resolution using the AILES Beamline of the SOLEIL synchrotron facility.¹

Platonic hydrocarbons, comprising dodecahedrane $(C_{20}H_{20})$ and cubane (C_8H_8) , are another family of hydrocarbon cages with additional interesting chemical properties. These species possess C–C bond angles that significantly deviate from the tetrahedral angle (109.8°) of the sp³ hybridized form of carbon, generating a considerable strain in the molecule. Cubane itself has the highest density of all hydrocarbons (1.29 g/cm³). This makes it able to store large amounts of energy, although the molecule is fully stable. As a matter of fact, cubane and its derivatives are studied to produce new compact materials for rocket engines, for instance. From the theoretical chemistry point of view, this is a very intriguing molecule, because of its high symmetry combined to these unique bonding properties. Eaton and Cole first synthesized cubane in 1964.^{2,3} Later on, Barborak and colleagues found an improved synthesis procedure.⁴ This molecule is a spherical-top with O_h octahedral symmetry. It possesses 18 (nondegenerate and degenerate) normal modes of vibration, among which only three (with F_{1u} symmetry) are infrared active and 8 are Raman-active. It should be noticed that for such centrosymmetric molecules, the infrared and Raman spectra are mutually exclusive: infrared bands have u parity, whereas Raman bands have g parity. Thus, both techniques are necessary for a complete spectroscopic characterization. Della and co-workers⁵ have recorded low-resolution spectra of C_8H_8 . The only existing high-resolution study is that of Pine et al.,⁶ who could record some parts of the three infraredactive fundamentals using diode lasers. These spectra were analyzed as isolated bands using a very simple phenomenological

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model. More recently, Vlahacos and co-workers⁷ or also Jursic⁸ and Karpushenkava et al.⁹ made theoretical studies of this molecule, using ab initio calculations.

We have chosen here to reinvestigate in detail the infrared spectrum of this molecule, thanks to the AILES beamline of the SOLEIL synchrotron facility. After a careful synthesis and characterization of our sample, we could record many high-resolution spectra over a wide spectral range. We performed a reanalysis of the ν_{11} and ν_{12} fundamentals, leading to new accurate effective Hamiltonian parameters. Thanks to new ab initio calculations it was also possible to assign many combination bands, that were never observed before.

Section II.A details the synthesis and characterization of our cubane sample. Section II.B presents the experimental infrared data. Our new quantum chemistry calculations are detailed in section II.C, and their results relative to the assignment of combination bands are presented in section III. Section III.A discusses the ground vibrational state rotational constant value. Sections III.B, III.C, and III.D present the assignment and analysis of the ν_{12} and ν_{11} fundamentals and discusses the highly perturbed structures of the ν_{10} C–H stretching region. Finally, section III.F compares our preliminary experimental results on combination bands with the literature data.

II. LABORATORY METHODS

II.A. Synthesis and Characterization. All details concerning the synthesis and characterization of our cubane sample realized by the Bari group are provided in Appendix A.

II.B. Infrared Spectroscopy. All spectra were recorded using the high-resolution Bruker IFS 125 Fourier transform interferometer located on the AILES beamline of the SOLEIL synchrotron facility together with the room temperature White type cell for which the optics were adjusted to obtain 150 m absorption path length. This setup has been already used several times in the past to obtain the IR and far-IR spectra of many relatively large C-bearing molecules, which are low vapor pressure solids at room temperature (such as, e.g., adamantane¹ and naphthalene¹⁰). The vibrational bands of cubane studied in this work span over a large frequency range $(600-3200 \text{ cm}^{-1})$ and exhibit large intensity differences (e.g., the intensity of the ν_{11} fundamental band is calculated to be about 4 km.mol⁻¹ and that of the ν_{10} fundamental band to be about 135 km.mol⁻¹). To provide a relatively complete description of the IR spectrum of cubane, we recorded six spectra with different experimental conditions listed in Table 1. Our spectra were calibrated using residual water absorption lines. We used the frequencies available from HITRAN database¹¹ concerning the H₂O ν_2 band.

Over this large range of experimental conditions, the rotational analysis of the ν_{11} and ν_{12} bands were obtained by using the conditions of spectrum 2. The very intense ν_{10} band (spectrum 3) was obtained at lower resolution (due to a larger Doppler broadening than for the ν_{11} and ν_{12} bands) and by reducing the pressure. Increasing the gas pressure allowed the detection of many combination bands (spectrum 4); their rotational analysis (using spectra 5 and 6) is still in progress and will be the subject of a next study.

Tabl	e 1.	Experimental	Conditions	Used	То	Record	Six	Infrarec	ł S	pectra	of	Cub	oane
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spectrum	pressure/ μ bar	$resolution/cm^{-1}$	no. of scans	iris/mm	beam splitter	windows	detector	high-freq filter	source
1	2	0.5	1000	4	KBr	ZnSe	MCT	no	synchrotron
2	3	0.001	300	1	KBr	ZnSe	MCT	no	synchrotron
3	0.7	0.003	80	1.15	KBr	ZnSe	InSb	3200	globar
4	16	0.5	1000	4	KBr	ZnSe	MCT	no	globar
5	16	0.0025	320	1.15	KBr	ZnSe	MCT	2400	globar
6	49	0.003	800	1.5	KBr	polypropylene	MCT	2400	globar

Table 2. Vibrational Wavenumbers (cm^{-1}) and IR Intensities (km/mol) with Several Theoretical Approaches^{*a*}

					experin	nental ^b	CC/Pople ^c	B3LYP/Dunning ^c		B3LYP/Pople ^c	
mode	sym ^d	deg ^e	type ^f	activity ^g	position	intensity	harmonic	harmonic	harmonic	IR Intensity	anharmonic
ν_1	A _{1g}	1	С-Н	R			3140	3125	3131	0	3001
ν_2	A _{1g}	1	C-C	R			1017	1016	1056	0	1040
ν_3	A_{2u}	1	С-Н	-			3102	3090	3094	0	2967
ν_4	A_{2u}	1	CCH	-			1005	1053	1013	0	995
ν_5	Eg	2	CCH	R			1117	1112	1113	0	1086
ν_6	Eg	2	C-C	R			912	912	910	0	897
ν_7	Eu	2	CCH	-			1142	1180	1174	0	1179
ν_8	E_u	2	CCC	-			600	624	624	0	609
ν_9	F_{1g}	3	CCH	-			1133	1165	1163	0	1147
ν_{10}	F_{1u}	3	С-Н	IR	2991	111	3119	3106	3113	135	2981
ν_{11}	F_{1u}	3	CCH	IR	1235	4	1260	1269	1267	4.2	1242
ν_{12}	F_{1u}	3	C-C	IR	852	10	863	867	862	10	850
ν_{13}	F _{2g}	3	С-Н	R			3113	3099	3105	0	2976
ν_{14}	F _{2g}	3	CCH	R			1204	1221	1218	0	1196
ν_{15}	F _{2g}	3	C-C	R			828	839	833	0	820
ν_{16}	F _{2g}	3	CCC	R			649	681	680	0	677
ν_{17}	F _{2u}	3	CCH	-			1066	1066	1066	0	1042
ν_{18}	F_{2u}	3	C-C	-	819		829	836	836	0	820

^aExperimental intensity values are estimated from the high-resolution spectra. ^bThis work. ^cPople's basis set is 6-311++G(2d,2p); the Dunning one is aug-cc-pVTZ. ^dIrreducible representation in the O_h point group. ^cDegeneracy. ^fC-H, C-C: stretching mode. CCH, CCC: bending mode. ^gIR: infrared. R: Raman. Other modes (–) are inactive, in first approximation.

II.C. Quantum Chemistry Calculations. Geometrical optimization and vibrational frequency calculations have been performed at two theoretical levels of theory: (1) the coupled-cluster singles and doubles excitations with perturbative triples method CCSD(T) and (2) the most popular hybrid density functional B3LYP. We have also used two basis sets of triple- ζ quality for each method, namely, the extended 6-311++G(2d,2p) basis set of Pople et al.,^{12,13} and the correlation consistent aug-cc-pVTZ basis set of Dunning et al.^{14,15} DFT calculations have been done using the Gaussian 09-RevA.02 package,¹⁶ whereas the CCSD(T) ones have been carried out with the Molpro code.¹⁷

To obtain a set of reference data, geometrical optimization has been performed at the CCSD(T)/aug-cc-pVTZ level. Vibrational frequencies have been calculated within the harmonic approximation using both CCSD(T) and B3LYP approaches and the 6-311++G(2d,2p) basis set. Vibrational frequency corrected for the anharmonic effect has been performed using second-order perturbative theory (as implemented in Gaussian 09 package) only with the B3LYP/6-311++G(2d,2p) method. To do this job, we slightly lowered the molecular symmetry. However, we carefully checked that the changes in energetic and harmonic vibrational frequencies are actually negligible. Some more details about the calculation output are given as Supporting Information to this paper.

Vibrational parameters are gathered in Table 2. Here again, we compare the harmonic theoretical results to those obtained at the CCSD(T)/aug-cc-pVTZ level. One can easily note that the B3LYP functional with both basis sets nicely reproduces the vibrational reference data (relative error <5%). Consequently, we can confidently use our theoretical anharmonic frequencies to compare with the experimental data.

II.D. Effective Hamiltonian. Cubane is a quite large octahedral spherical top molecule. Its point group symmetry at equilibrium is O_h . It possesses 18 distinct normal modes of vibration: 4 nondegenerate mode with A_{1g} or A_{2u} symmetry, 4 doubly degenerate mode with E_g or E_u symmetry and 10 triply degenerate modes with $F_{1g'}$ $F_{1u'}$ $F_{2g'}$ or F_{2u} symmetry.^{5–9} In the first approximation, only F_{1u} fundamentals are infrared

active, that is, only ν_{10} , ν_{11} , and ν_{12} . Eight modes are Raman-only active (infrared absorption and Raman scattering spectra, being, in this sense, mutually exclusive). Again, in the first approximation, the seven remaining modes are inactive. We show below, however, that some of these can be slightly active through rovibrational interactions with the active modes. Table 2 summarizes the normal modes of cubane, together with their observed and calculated frequencies from the present work (section II.C).

To analyze the spectra, we use the formalism developed in Dijon for spherical top molecules. This one is based on group theory and tensorial formalism methods as already described in refs 18–20. This formalism allows a systematic expansion of the Hamiltonian and transition moment operators up to a given order and for any vibrational level or polyad (group of interacting vibrational levels).

In the present case, we simply consider isolated fundamental bands (ν_{11} and ν_{12}) in detail. Thus, we only need simple effective Hamiltonian operators:

• The ground state (GS) effective Hamiltonian:

$$\tilde{H}^{\langle \text{GS} \rangle} = \tilde{H}^{\langle \text{GS} \rangle}_{\{\text{GS}\}} \tag{1}$$

• The ν_i (*i* = 11 or 12) effective Hamiltonian:

$$\tilde{H}^{<\nu_i>} = \tilde{H}^{<\nu_i>}_{\{GS\}} + \tilde{H}^{<\nu_i>}_{\{\nu_i\}}$$
(2)

Table 3. Cubane Structural Parameters from This Work and from the Literature: Bond Lengths ($r_{\rm CC}$ and $r_{\rm CH}$), Band Center ($\tilde{\nu}$), Rotational (B_e and B_0), Centrifugal Distorsion (D_c) and Corielis (\hat{r}) Constants

		equilibrium				ground state			$ \nu_{11} = 1 $			$ u_{12} = 1 $	
	$r_{\rm CC}/{ m pm}$	$r_{ m CH}/ m pm$	$B_{\rm e}/{ m cm}^{-1}$	$r_{\rm CC}/{ m pm}$	$r_{ m CH}/ m pm$	B_0/cm^{-1}	$D_0/10^{-9}{ m cm}^{-1}$	${ ilde { ilde { u}}}^{-1}$	$\Delta B/\mathrm{cm}^{-1}$	s,	${ ilde v}/{ m cm}^{-1}$	$\Delta B/\mathrm{cm}^{-1}$	r
this work (experiment)						0.111195 (fixed)	6.14274 (fixed)	1234.915819(50)	$4.9694(41) \times 10^{-5}$	0.220	851.779972(45)	$1.46088(91) \times 10^{-4}$	-0.213
this work (calculation)	156.9	108.6	0.112194	157.6	109.1	0.111195	6.14274	1242	4.84×10^{-5}	0.228	850	1.799×10^{-4}	-0.217
Cole et al. ²²						0.1168		1234.760(2)	$5.00(6) \times 10^{-5}$		851.279(8)	$0.773(4) \times 10^{-4}$	
Pine et al. ⁶						0.1122(2)		1234.86714(3)	$4.9528(90) \times 10^{-5}$		851.82750(5)	$1.394(31) \times 10^{-4}$	
Almenningen et al. ²⁴				157.5(1)	110.0(6)	0.111122							
Hedberg et al. ²⁵	157.1(2)	109.6(1)	0.111712	157.3(2)	111.4(66)	0.111105							
Hirota et al. ²³				157.08	109.70	0.111719	6.0372						

Table 4	Effective	Hamiltonian	Parameters	for	the $\nu_{\rm ex}$	and ν .	. Fundamental	Bands ^a
I aDIC T	Linecuve	Trainittoman	1 arameters	101	$me \nu_{12}$	and ν_1	1 Fundamental	Danus

$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	vibrational level	order	$\Omega(K,nC)$	$\nu_{12}/{\rm cm}^{-1}$	$\nu_{11}/{ m cm}^{-1}$	"usual" notation ^{18,41}
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	v = 0	0	$2(0_{g}0A_{1g})$	1.11195×10^{-1}	1.11195×10^{-1}	B_0^{b}
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	v = 0	0	$4(0_{g'}0A_{1g})$	$-6.14274054 \times 10^{-9}$	$-6.14274054 \times 10^{-9}$	$-D_0^{b}$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\nu = 1$	0	$0(0_{g'}0A_{1g})$	851.779972(45)	1234.915819(50)	ν (band center)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\nu = 1$	1	$1(1_{g'}0F_{1g})$	$-1.004323(29) \times 10^{-1}$	$1.038828(21) \times 10^{-1}$	$3\sqrt{2}B\zeta$ (Coriolis)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\nu = 1$	2	$2(0_{g'}0A_{1g})$	$1.46088(91) \times 10^{-4}$	$4.9694(41) \times 10^{-5}$	$B_{\rm v} - B_0$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\nu = 1$	2	$2(2_{g'}0E_{g})$	$8.645(12) \times 10^{-5}$	$-1.00148(42) \times 10^{-4}$	$-(1/2)\alpha_{220} - 6\alpha_{224}$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\nu = 1$	2	$2(2_{g'}0F_{2g})$	$-1.4024(19) \times 10^{-4}$	$1.06978(25) \times 10^{-4}$	$-(3/4)\alpha_{220} + 6\alpha_{224}$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\nu = 1$	3	$3(1_{g'}0F_{1g})$	$-3.2116(68) \times 10^{-7}$	$-1.311(27) \times 10^{-8}$	$-(3\sqrt{3}/4\sqrt{2})F_{110}$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\nu = 1$	3	$3(3_{g'}0F_{1g})$	$-3.9823(48) \times 10^{-7}$	$-6.14(20) \times 10^{-9}$	$(3/\sqrt{5}/2)F_{134}$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\nu = 1$	4	$4(0_{g},0A_{1g})$	$-3.89(51) \times 10^{-10}$	$-2.351(73) \times 10^{-10}$	$-(D_{\rm v}-D_0)$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\nu = 1$	4	$4(2_{g'}0E_{g})$	$-7.14(27) \times 10^{-10}$	$-6.51(53) \times 10^{-11}$	$(\sqrt{3}/8)G_{220} + (3\sqrt{3}/2)G_{224}$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\nu = 1$	4	$4(2_{g}OF_{2g})$	$1.55(55) \times 10^{-10}$	0.0 ^b	$(3\sqrt{3}/16)G_{220} - (3\sqrt{3}/2)G224$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\nu = 1$	4	$4(4_{g}OA_{1g})$	$-3.001(77) \times 10^{-10}$	$-3.092(85) \times 10^{-11}$	$-(3\sqrt{5}/4\sqrt{2})(D_{vt}-D_{0t})$
$ \begin{array}{ccccc} \nu = 1 & 4 & 4(4_{g0}0F_{2g}) & 3.087(14) \times 10^{-9} & 0.0^{b} & -(9\sqrt{7}/8)G_{244} - (\sqrt{21}/\sqrt{22})G_{246} \\ \nu = 1 & 5 & 5(1_{g0}0F_{1g}) & 2.736(46) \times 10^{-12} \\ \nu = 1 & 5 & 5(3_{g0}0F_{1g}) & -4.2(1.2) \times 10^{-13} \end{array} $	$\nu = 1$	4	$4(4_{g}, 0E_{g})$	$1.263(12) \times 10^{-9}$	$-1.222(68) \times 10^{-10}$	$-(3\sqrt{7}/2)G_{244} + (\sqrt{21}/2\sqrt{22})G_{246}$
$ \begin{array}{ccccc} \nu = 1 & 5 & 5(1_g 0 F_{1g}) & 2.736(46) \times 10^{-12} \\ \nu = 1 & 5 & 5(3_g 0 F_{1g}) & -4.2(1.2) \times 10^{-13} \end{array} $	$\nu = 1$	4	$4(4_{g}0F_{2g})$	$3.087(14) \times 10^{-9}$	0.0 ^b	$-(9\sqrt{7}/8)G_{244} - (\sqrt{21}/\sqrt{22})G_{246}$
$\nu = 1$ 5 $5(3_{g0}0F_{1g})$ $-4.2(1.2) \times 10^{-13}$	$\nu = 1$	5	$5(1_{g}0F_{1g})$	$2.736(46) \times 10^{-12}$		
	$\nu = 1$	5	$5(3_{g'}0F_{1g})$	$-4.2(1.2) \times 10^{-13}$		
$\nu = 1$ 5 $5(5_{gg}0F_{1g})$ $-1.34(13) \times 10^{-12}$	$\nu = 1$	5	$5(5_{g'}0F_{1g})$	$-1.34(13) \times 10^{-12}$		
assignments 4909 3767	assignments			4909	3767	
J _{max} 90 84	$J_{\rm max}$			90	84	
$d_{\rm rms}/10^{-3} {\rm ~cm}^{-1}$ 0.322 0.378	$d_{\rm rms}/10^{-3}~{\rm cm}^{-1}$			0.322	0.378	

"One standard deviation is indicated in parentheses, in the unit of the last two digits, for fitted parameters. ^bFixed value (see text).

which contains both the ground state and $\nu_i = 1$ operators and parameters.

As discussed later in section III, the case of the ν_{10} C–H stretching region appears more complex, the ν_{10} fundamental band being obviously in strong interaction with some other vibrational levels. This problem will be the subject of a future work. The different terms in the above effective Hamiltonians are written in the form:

$$\tilde{H}_{\{\mathrm{GS}\,\mathrm{or}\,\nu_{i}\}}^{<\nu_{i}>} = \sum_{\mathrm{allindexes}} t_{\{s\}\{s'\}}^{\Omega(K,n\Gamma)\Gamma_{\nu}\Gamma_{\nu}'} \beta({}^{\varepsilon}V_{\{s\}\{s'\}}^{\Omega_{\nu}(\Gamma_{\nu}\Gamma_{\nu}')\Gamma} \otimes R^{\Omega(K,n\Gamma)})^{(\mathrm{A}_{\mathrm{lg}})}$$

$$(3)$$

In this equation, the $t_{\{s\}\{s'\}}^{\Omega(K,n\Gamma)} \Gamma_v \Gamma_v'}$ are the parameters to be determined, whereas ${}^{e}V_{\{s\}\{s'\}}^{\Omega_v(\Gamma_v \Gamma_v')\Gamma}$ and $R^{\Omega(K,n\Gamma)}$ are vibrational and rotational operators of respective degree Ω_v and Ω . Their construction, based on symmetrized polynomials of the elementary rotational angular momentum and creation and annihilation operators for each normal mode, is described in ref 18. β is a factor that allows the scalar terms ($\Gamma = A_{1g}$) to match the usual terms like $B_0 J^2$, etc. The symbol \otimes represents the tensorial (coupling) product. The order of each individual term is defined as $\Omega + \Omega_v - 2$. Let us also notice that we have here s = s' = GS or ν_i only.

To compute line intensities and to obtain simulated spectra, the dipole moment operator is expanded in the same way. The reader is referred for instance to refs 18 and 21 for general details about its construction. This time, the order of the development in our model is defined as $\Omega + \Omega_v - 1$. In the present case, because we do not consider absolute line intensities, the effective dipole moment is expanded up to order zero only, resulting into a single parameter for each fundamental band, whose value is arbitrarily set to 1.

Finally, we use here a vibrational basis set restricted to the $\nu_i = 1$ level:

$$|\Psi_{\mathbf{v}}\rangle = |\Psi_{\nu_{i}=1}^{(l_{i}=1,\mathbf{F}_{1a})}\rangle \tag{4}$$

i.e., we use a three-dimensional oscillator with vibrational angular momentum quantum number l_i and O_h symmetry F_{1u} . The Hamiltonian and dipole moment matrix elements are calculated in the coupled rovibrational basis set:

$$|\Psi_{\rm rv}\rangle = |(\Psi_{\nu_{\rm i}=1}^{(l_{\rm i}=1,{\rm F}_{\rm iu})} \otimes \Psi_{\rm r}^{(l_{\rm g},n{\rm C}_{\rm r})})^{({\rm C}={\rm F}_{\rm iu}\otimes{\rm C}_{\rm r})}\rangle$$
(5)

 $\Psi_r^{(J,nC_r)}$ being a rotational wave function with angular momentum quantum number *J* (considered to have g parity), rotational symmetry species C_r and multiplicity index *n* (see ref 18), whereas C is the overall rovibrational symmetry species.

III. RESULTS AND DISCUSSION

III.A. Ground State Rotational Constants. In the case of an isolated infrared-active triply degenerate fundamental band of a spherical-top molecule, it is not possible to simultaneously fit the ground and excited vibrational state rotational constant, due to strict selection rules that forbid combination differences. Such a molecule has no permanent dipole moment and, moreover, strictly no pure rotational lines because of the parity selection rule for such a molecule with a center of symmetry. It is thus necessary to fix the ground state rotational constants to some value. We choose here to expand $\tilde{H}^{<GS>}$ up to order 2 only, retaining only scalar parameters, namely, the rotational constant B_0 and the centrifugal distortion constant D_0 .

Concerning B_0 , different values derived from calculations or previous experimental results are summarized in Table 3. Cole et al.,²² Pine et al.,⁶ and Hirota et al.²³ published rotational constants obtained from gas phase spectroscopy, and Almenningen et al.²⁴ and Hedberg et al.²⁵ derived the GS rotational constants from electron diffraction measurements. The most accurate experimental determination of the rotational constant B_0 has been published by Hedberg et al.²⁵ It associates gas phase electron diffraction measurements with numerous experimental results and, in particular, with very accurate GS pure rotation spectroscopy of mono deuterated cubane.²³



Figure 1. Overview of the ν_{12} fundamental band, compared to the simulation. The bottom panel displays the fit residuals for line positions.



Figure 2. Detail in the P branch of the ν_{12} fundamental band, compared to the simulation. The bottom panel displays the fit residuals for line positions. Some cluster line symmetries are indicated in the case of the P(51) lines (parity index is omitted).

In the present work, the molecular structure optimized in our quantum chemistry calculations are in very good agreement with the experimental values from Hedberg et al.²⁵ Two geometrical parameters, C–C = 157.4 pm and C–H = 108.8 pm at the equilibrium configuration, calculated at the CCSD(T)/ aug-cc-pVTZ level are well reproduced with CCSD(T)/ 6311++G(2d,2p) [157.8 and 109.4 pm], B3LYP/aug-cc-pVTZ [156.8 and 108.6 pm], and B3LYP/6-311++G(2d,2p) [156.9 and 108.6 pm] methods. The corresponding relative error is less than 1%. These parameters agree well with the r–g structure (vibrationnally averaged) from Hedberg et al.²⁵ (Table 3). In the same way, our D_0 centrifugal distortion constant agrees well with that of Hirota et al.²³

Therefore, to compare the variation of rotational constants between the ground and excited states studied here (α matrix),

we have chosen to use the rotational constant B_0 and the centrifugal distortion constant D_0 obtained from our calculations.

III.B. ν_{12} **Band.** The ν_{12} fundamental band displays a clear P, Q₁ and R branch structure with well-resolved line clusters for each J value. Its assignment and analysis is quite straightforward. $\tilde{H}^{<\nu_{12}>}$ was expanded up to order 5. A total of 4909 transitions could be assigned up to J = 90. All 16 effective Hamiltonian parameters could be fitted with a small standard deviation. The overall root-mean-square deviation is 0.278 × 10^{-3} cm⁻¹. This result is comparable to that of Pine et al.,⁶ although we could assign considerably (more than six times) more transitions. We get more effective Hamiltonian parameter values (adding that these authors fitted more phenomenological transition parameters). The resulting effective Hamiltonian parameters are given in Table 4. As shown in Table 3, the ΔB

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Figure 3. Overview of the ν_{11} fundamental band, compared to the simulation. The bottom panel displays the fit residuals for line positions.



Figure 4. Detail in the R branch of the ν_{11} fundamental band, compared to the simulation. The bottom panel displays the fit residuals for line positions. Some cluster line symmetries are indicated in the case of the R(42) lines (parity index is omitted).

and ζ Coriolis parameter values for ν_{12} obtained from the anharmonic calculations agree very well with the experimental ones.

Figure 1 shows an overview of the ν_{12} fundamental band, compared to the simulation, along with the fit residuals for line positions. These are well distributed between $\pm 2 \times 10^{-3}$ cm⁻¹ with no systematic deviation as *J* increases (toward the ends of the branches), showing the consistency and completeness of the model we use. Some saturation occurs for the strongest Q branch lines, resulting in artifacts in the absorbance calculation. This did not prevent us, however, to assign many Q lines.

Figure 2 shows a detail in the R(50) to R(52) region, compared to the simulation and along with some examples of assignments of line clusters in the form of the ground state symmetry

 $(O_h$ point group irreducible representations; the parity index, which is g, is omitted for sake of clarity). As for all heavy spherical-top molecules, lines appear to cluster as it has been observed and explained in many other cases.^{26–32}

III.C. ν_{11} **Band.** The ν_{11} fundamental band also displays a clear and well-resolved P, Q, and R branch structure. A total of 3767 transitions could be assigned up to J = 84. $\tilde{H}^{<\nu_{11}>}$ needs to be expanded up to order 4 only. Eleven effective Hamiltonian parameters could be fitted with a small standard deviation, the two remaining parameters being nondeterminable and thus fixed to zero. The overall root-mean-square deviation is 0.350×10^{-3} cm⁻¹. Again, this result largely extends that of Pine et al.⁶ The resulting effective Hamiltonian parameters are also given in Table 4. As for ν_{12} , the comparison of observed and calculated ΔB and ζ constants for ν_{11} is very satisfying (Table 3).



Figure 5. Q branch of the ν_{11} fundamental band, compared to the simulation. The bottom panel displays the fit residuals for line positions.



Figure 6. Experimental spectrum of the ν_{10} fundamental band. The insets show details in the P and R branches.

Figure 3 shows an overview of the ν_{11} fundamental band, compared to the simulation, along with the fit residuals for line positions.

Although the octahedral splitting is in this case quite large, so that there is an overlap between successive J values, the structure remains well resolved.

Figure 4 shows a detail in the R(40) to R(43) region, compared to the simulation and along with some examples of assignments of line clusters (as for ν_{12} , see Figure 2 above). Figure 5 displays the very characteristic structure of the Q branch, which also could be largely assigned, despite a very high line density.

III.D. ν_{10} **C–H Stretching Region.** As already noticed by Pine et al.,⁶ the ν_{10} C–H stretch fundamental band displays a complex and highly perturbed structure. As we can see in Figure 6, *J* clusters cannot be easily recognized and distinguished in the

P and R branches. Contrary to the two previous bands, no straightforward assignment can be performed. Considering Table 2, the most likely perturber is the nearby ν_3 nondegenerate fundamental band with A2u summetry (only vibrational levels with u parity can interact in the infrared absorption spectrum of a centrosymmetric molecule). Literature values situate this band a few cm⁻¹ apart from ν_{10} , although no precise determination exists at present. Thus, quadratic Coriolis interaction of type $t_{\{\nu_{10}\}\{\nu_{3}\}}^{2(2,0F_{2g})}$ $F_{1u}A_{2u}$ is very likely to occur between the $\nu_{10} = 1$ and the $\nu_3 = 1$ vibrational levels, forming a closely interacting dyad. The first attempts to include such an interaction, although leading to a quite similar overall structure of this region proved to be unsuccessful to allow detailed assignments. Further investigations are still needed, from the theoretical side, to estimate initial rovibrational parameters. This will be the subject of a future work.

III.E. Infrared Intensities. Taking into account the optical path length and gas pressure (see section II.B and Table 1), we estimated integrated band intensities using both high-resolution (rotationally resolved) and low-resolution spectra. Both estimations agree well. These intensities for the three active fundamental modes are in excellent agreement with the calculated values as shown in Table 2.

III.F. Combination Bands and "Forbidden" Bands. The above-described anharmonic quantum chemistry calculations allow to identify some combination bands, although some ambiguities remain. It should be recalled that, for such a centro-symmetric molecule, only combination bands with u parity can be observed in infrared dipolar absorption. Moreover, only those featuring a vibrational sublevel with F_{1u} symmetry can display a significant intensity. Our spectra show many of these combination bands, all of them displaying a nicely resolved rovibrational structure. Figure 7 shows six regions for which bands of group of

bands (polyads) can be identified when comparing to calculations.

We can notice a very unusual intensity pattern with abnormally strong lines in the P branch region of the ν_8 + ν_{16} combination band. This is likely to be quite similar to what we previously observed in the case of the ν_{25} fundamental band of adamantane.¹ It is thus probably due to a Coriolis interaction with a nearby rovibrational band, yet to be identified. The ν_{11} fundamental level is a plausible candidate, although it does not seem to be perturbed in the present analysis (see above). But, as a matter of fact, in the case of adamantane, the ν_{24} perturber also has itself a regular structure and lies at a similar wavenumber distance of ca. 40 cm⁻¹. For cubane, the detailed analysis of $\nu_8 + \nu_{16}$ is, however, not yet possible, because this necessitates knowledge of the $\nu_8(E_u)$ and $\nu_{16}(F_{2g})$ fundamental bands themselves and a good estimate of the position of the two vibrational sublevels of the combination level (there are two sublevels, because $E_u \otimes F_{2g} = F_{1u} \oplus F_{2u}$.



Figure 7. Experimental spectra of the various combination bands. Insets show details of the resolved rovibrational structure.

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Table 5. Some Calculated and Observed Vibrational Bands of Cubane

spectral region	bands	calculated (anharmonic)/cm ⁻¹	observed band centers/cm ⁻¹
		Fundamental Bands	
814-821	ν_{18}	820.2	819
830-880	ν_{12}	849.7	851.8
1220-1250	$ u_{11} $	1241.8	1234.9
2960-3020	ν_{10}	2980.9	2991
		Combination Bands	
1265-1290	$\nu_8+\nu_{16}$	1286.0	1275.3
1620-1645	$\nu_{15}+\nu_{18}$	1639.6	1634.8
1680-1780	$\nu_6+\nu_{18}$	1715.7	
	$\nu_4+\nu_{16}$	1716.7	
	$\nu_{16}+\nu_{17}$	1718.3	(1715.4, 1716.7, 1749.4)
	$\nu_6+\nu_{12}$	1745.9	
	$\nu_8 + \nu_9$	1755.1	
1780-1860	$\nu_8+\nu_{14}$	1804.7	
	$\nu_2+\nu_{12}$	1843.9	
	$\nu_7+\nu_{16}$	1856.8	(1824.6, 1857.8)
	$\nu_4+\nu_{15}$	1860.6	
	$\nu_{15}+\nu_{17}$	1863.1	
1880-2040	$\nu_5+\nu_{18}$	1905.2	
	$\nu_{16}+\nu_{11}$	1917.9	
	$\nu_5+\nu_{12}$	1934.8	
	$\nu_6+\nu_{17}$	1939.4	
	$\nu_9+\nu_{18}$	1965.9	
	$\nu_9+\nu_{12}$	1995.6	(1904.9, 1955.8, 1979.3, 2011.0)
	$\nu_7 + \nu_{15}$	1917.9	
	$\nu_{14} + \nu_{18}$	2015.6	
	$\nu_{12} + \nu_{14}$	2045.3	
	$\nu_{11} + \nu_{12}$	2062.4	
2360-2380	$\nu_7+\nu_{14}$	2347.7	2369

Beyond these general qualitative comments, it is clear, however, that a detailed assignment and fit of rovibrational effective Hamiltonian for these bands is still a very difficult task. It will require first a better knowledge of all fundamental bands implied in the present combinations. This is complicated by the fact that most of the fundamentals are not active in infrared absorption (Table 2). High-resolution Raman spectroscopy could be of great help in some cases, as already proved by our previous works on the SF₆ molecule.^{33–36}

Some other "forbidden" fundamental bands may also be observed through rovibrational interactions, making them slightly active. This is the case of at least ν_{18} whose Q branch is slightly visible in our spectra around 819 cm⁻¹ (estimated value from a very preliminary tentative simulation of the Q branch). This case is fully similar to that of the ν_6 fundamental band of SF₆, with the same F_{2u} symmetry and that was recently observed at the AILES beamline of the SOLEIL synchrotron facility.³⁷

Table 5 summarizes the different fundamental and combination band (or combination band regions in case of complex polyads) that can be observed in our spectra (Figure 7), compared with anharmonic calculations.

IV. CONCLUSION AND PERSPECTIVES

After a careful synthesis and characterization of a sample of the cubane molecule, we reinvestigated the high-resolution spectrum of this molecule over a wide spectroscopic range. We could significantly improve the detailed rovibrational assignment and analysis of the ν_{11} and ν_{12} fundamental bands. Many other combination bands were also recorded for the first time, displaying a nicely resolved rovibrational structure in each case. Anharmonic quantum chemistry calculations have been performed to help the identification of several bands. In a near future, an important effort will be devoted to the spectral analysis of these combination bands that might provide new information on the structure and force field of this peculiar molecule in its electronic ground state. As shown in the previous sections, the ΔB values of ν_{11} and ν_{12} obtained from the anharmonic calculations agrees very well with the experimental one (within few 10^{-5} cm⁻¹). This further confirms the quality of the calculations to predict spectroscopic parameters for the GS and fundamental bands. The anharmonic calculations provides ΔB estimates for the other fundamental bands (slightly IR active through rovibrational interactions) and also for combination bands and overtones. As it was used recently to study numerous IR and far-IR band of large aromatic molecules,³⁸ the accuracy of these estimates might be an invaluable support to forthcoming spectral analysis of the rotational structures observed in many combination modes.

APPENDIX A: SYNTHESIS AND CHARACTERIZATION

1. Materials and Methods

Melting points were not corrected. GC/MS experiments were run using a ZB-1 column (30 m × 0.25 μ m id); the MS were performed in EI mode (70 eV). The ¹H NMR spectra were recorded on a 500 MHz NMR spectrometer; resonances are referenced to residual isotopic impurity CHCl₃ (7.26 ppm) of solvent CDCl₃ and/or to TMS. The ¹³C NMR spectral data



Figure 8. Cubane synthesis scheme.



Figure 9. ¹H (top panel) and ¹³C (bottom panel) NMR spectra of the cubane sample.





(125.76 MHz) are referenced to the middle peak of CDCl_3 solvent (77.0 ppm).

2. Preparation and Characterization

Cubane is a white solid. Its melting point is ca. 130–133 °C; purity >98% GC. It was synthesized upon decarboxylation of 1,4-cubanedicarboxylic acid (melting point 226 °C) by a literature procedure (Figure 8).³⁹

Figures 9 and 10 show the NMR and mass spectra of the resulting sample, respectively. Theses spectra are in good agreement with the data reported by Della *et al.*⁴⁰

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