

Ab initio characterization of C₅

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In this paper, the structure and spectroscopic parameters of the C₅ cluster are determined using multiconfigurational quantum chemical methods as implemented in the MOLCAS software. A number of spectroscopic properties (band center positions, *l*-doubling parameters, and rotational constants) have been characterized. From the new results, the assignments of previous astrophysical observations [J. Goicoechea *et al.*, *Astrophys. J.* **609**, 225 (2004)] are discussed. A detailed exploration of the global potential energy surface confirms that C₅ has a X¹Σ_g⁺ linear isomer of prominent stability and, at least, three minimum energy structures showing singlet electronic ground states. Two of them are cyclic and one has a nonplanar geometry. Vertical and adiabatic electronic transitions and vibrational spectroscopic parameters are determined for the most stable linear isomer using multiconfigurational second order perturbation theory (CASPT2) using an active space containing 12 valence orbitals with 12 active electrons and extended ANO-type basis sets. The infrared spectrum has been analyzed from an anharmonic force field derived from the local surface, determined from the energies of a grid of 1350 geometries. The force field includes four coupling terms. The CASPT2 band center position of the ν₇(π_u) anharmonic fundamental has been calculated to be at 102 cm⁻¹, which validates the assignment to C₅ of the pattern of bands centered at 102 cm⁻¹ observed with the ISO telescope. © 2007 American Institute of Physics. [DOI: 10.1063/1.2759206]

INTRODUCTION

C_{*n*} carbon chains are relevant species for astrophysics, since they have been proposed as responsible of the diffuse interstellar bands,¹ and they play an important role in the reactivity of polycyclic aromatic hydrocarbons.²

One of the smallest homonuclear chain, C₅, has been observed in the interstellar medium (ISM),³ even if its astrophysical detection is not straightforward and contains numerous obstacles: its abundance in the ISM is very low;⁴ as homonuclear cluster, it cannot be detected through the rotational lines with radio telescopes, and the characterization has to be based on electronic or vibrational transitions. Furthermore, few sources (especially in the ISM) have enough flux at 2000 cm⁻¹ to allow systematic studies of the ν₃(σ_u) infrared active stretching mode.³ For these objects, only far infrared techniques through antisymmetric bending modes can be applied.

The present work has been initialized motivated by the recent observations of the Molecular Astrophysics Group of Madrid,⁵ who have observed with the Infrared Space Observatory an unidentified band at very low frequency (102 cm⁻¹) in the carbon rich young planetary nebula NGC 7027. The band appears to be composed of several peaks lying at 108.93, 107.76, 106.50, 105.04, 102.46, 101.11,

99.50, and 98.33 cm⁻¹ and presents a shape that cannot be reproduced by atomic fine-structure lines, recombination lines, or the rotational emission of abundant molecules. By taking into consideration the chemical properties of the astrophysical object, some peaks can be attributed to small carbon chains. Strong reasons justified its assignment to C₅ or to C₆.⁵ At present, which of this two species is the responsible for the band cannot be deduced from the existing information.

Little information is available for the smallest carbon chains, in spite of the fact that larger molecules, such as the fullerenes, are well known. With the exception of C₃,² the band origin of the other C_{*n*} bending modes has not been accurately determined, and there is disagreement between values for the C₄, C₅, and C₆ fundamentals obtained from different techniques. As C_{*n*} clusters are chemical species of relatively low stability, the determination of many of their properties using experimental techniques is unfeasible, and the use of theoretical methods represents a viable alternative to obtain such data.^{6,7} For this reason, we provide in this paper a description of the electronic and vibrational transitions emphasizing the far infrared bending modes. We employ, for this purpose, the CASPT2 method (multiconfigurational second order perturbation theory)⁸ implemented in the MOLCAS package.⁹ The use of such an approach seems necessary considering the multiconfigurational nature of the ground state wave function.

The review of Van Order and Saykally¹⁰ provides a de-

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tailed report of previous studies performed on the smallest C_n clusters for the past years. C_5 was first detected in IRC +10216 in 1989, based on the location of a $\nu_3(\sigma_u)$ infrared band centered at 2169.44 cm^{-1} .³ The assignment was confirmed by laboratory diode laser absorption spectroscopy of supersonic carbon cluster beams.¹¹ In 1988, the assignment of a band observed at 2164 cm^{-1} with IR spectroscopy in an Ar matrix made it possible to identify the molecule.¹² This band had previously been assigned to C_4 (Refs. 13 and 14) and was reassigned to the $\nu_3(\sigma_u)$ mode of C_5 on the basis of the *ab initio* calculations of Raghavachari and Binkley performed at the Hartree-Fock level.¹⁵ These authors have also studied the isomers of the cluster and have given the first relation of the stable structures.

Recently, Moazzen-Ahmadi *et al.*^{16,17} have measured the absorption spectrum of $\nu_3(\sigma_u)$ with a diode laser spectrometer. The assignments of the observed patterns provide many new molecular parameters, such as the rotational constant ($B_0=2557.63\text{ MHz}$) and the l -doubling constants q_7 and q_5 , computed from the analysis of associated hot bands.

As can be expected, the strongest infrared active $\nu_3(\sigma_u)$ mode represents the most well known vibration of C_5 . With few exceptions, the remaining modes are not so well known. Moazzen-Ahmadi *et al.*^{16,17} have determined the band positions of the large amplitude bending vibrations $\nu_7(\pi_u)$ and $\nu_5(\pi_u)$ at 118 ± 3 and $218\pm 13\text{ cm}^{-1}$ with diode laser spectroscopy. From Fourier-transform IR in an Ar matrix, Kranze and Graham¹⁸ have assigned the band observed at 1446.6 cm^{-1} to the $\nu_4(\sigma_u)$ mode; Szczepanski *et al.*¹⁹ have assigned $\nu_2+\nu_3$ and $2\nu_3$ to bands at 2939.9 and 4327.8 cm^{-1} , observed with IR spectroscopy of matrix-isolated carbon clusters; and with anion photoelectron spectroscopy, Arnold *et al.*²⁰ have determined the $2\nu_5$, $2\nu_6$, and $2\nu_7$ overtones and the $\nu_2(\sigma_g)$ symmetric stretching fundamental to be at 444 , 1024 , 202 , and $798\pm 45\text{ cm}^{-1}$, respectively. Kitsopoulos *et al.*²¹ provide band center positions for three fundamentals, $\nu_2=779\text{ cm}^{-1}$, $\nu_5=216\text{ cm}^{-1}$, $\nu_6=535\text{ cm}^{-1}$, and $\nu_7=106\text{ cm}^{-1}$ from photodetachment spectroscopy measurements.

Major studies of the electronic absorption spectra of carbon chains come from Maier *et al.*²² Forney *et al.*²³ have identified the ${}^1\Sigma_u^+ \leftarrow X\text{ }{}^1\Sigma_g^+$ spectrum of C_5 trapped in 5 K neon matrices. They provide the position of the ${}^1\Pi_u^+ \leftarrow X\text{ }{}^1\Sigma_g^+$ transition predicted to occur at 428 nm by Kolbuszewski²⁴ using *ab initio* calculations. The vertical excitations were also investigated by Pachionni and Koutecky²⁵ with theoretical procedures.

Most of these assignments are based on previous *ab initio* calculations performed within the harmonic approximation. To our knowledge, only the paper of Botschwina and Sebald²⁶ describes anharmonic effects using large-scale CEPA-1 calculations. They focus in the stretching modes predicting a ν_3 anharmonic fundamental centered at 2301 cm^{-1} , with a high transition moment (0.74 D). Harmonic fundamentals have been computed by Martin *et al.*²⁷ at the MP2/6-31G** level and Kurtz and Adamowicz²⁸ with MBPT and coupled-cluster calculations. Later studies using second order perturbation theory, density functional theory, and CCSD(T) have been performed by Kurt and

Adamowicz,²⁹ Hutter *et al.*,³⁰ Botschwina,³¹ and Martin and Taylor.³² The ionization potential and the structural properties of the ionic species have been studied with the one-particle Green's function approach³³ and also with MRCI *ab initio* calculations.³⁴ Nonlinear properties have been also investigated using DFT methods.^{35,36}

THEORETICAL APPROACH

The determination of the structural parameters and vertical and adiabatic excitation energies of linear- C_5 has been performed using the CASPT2/CASSCF method^{8,37} implemented in the MOLCAS package,⁹ an active space containing 12 valence orbitals with 12 active electrons and the ANO-L ($4s3p2d1f$) basis set.³⁸ Band positions and spectroscopic parameters corresponding to the electronic ground state have been calculated using classical perturbation theory and the code FIT-ESPEC.³⁹ For this purpose, an anharmonic force field has been computed by fitting to a local full-dimensional potential energy surface the CASPT2/CASSCF/ANO-L ($3s2p1d$) energies of a grid of 1350 geometries.

A preliminary search of the minimum energy geometries of C_5 has been performed at the B3LYP level of theory.

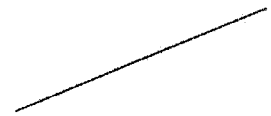
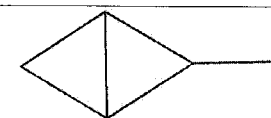
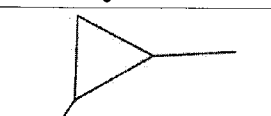

RESULTS AND DISCUSSION

Neutral C_n carbon clusters display isomerism¹⁰ and behavior depending on the parity of n .¹⁰ Chains with odd n , such as C_5 , present a favored linear isomer which ground electronic state is a singlet. However, chains with even n , as is the case of C_4 ,⁶ show at least two isomers of similar stability, one linear and one cyclic. In this last case, the linear isomer is always the one that is observed experimentally and present a triplet electronic ground state. All the isomers can act as intermediates in reactions in gas phase although most of previous measured and calculated properties correspond to the linear structures. The isomerization processes are not well known.

The first *ab initio* structural study of C_5 was performed with MP4/6-31G(d) calculations by Raghavachari and Binkley,¹⁵ who found one linear isomer, one cyclic isomer, and a stable trigonal bipyramidal geometry, analogous to the ground state structure for Si_5 , lying at 60 and 95 kcal/mol above the linear structure, respectively. Unfortunately, to our knowledge, the detailed description of these isomers is not available and later studies have focused on the linear isomer neglecting the cyclic and nonplanar forms. Here, we have performed a search of the potential energy surface using B3LYP/aug-cc-pVTZ theory as a preliminary description of the cluster. Table I represents a brief relation of structural and spectroscopic parameters, dipole moment, and rotational constants of the most characteristic isomers. Positive harmonic frequencies confirm the character of minimum of the stationary points.

As was expected, the stability of the favorite linear form, $X\text{ }{}^1\Sigma_g^+$, is really significant. The remaining isomers, which ground electronic state is always a singlet, are two planar structures of C_{2v} symmetry, $c\text{-}C_5$ and $t\text{-}C_5$, and a nonplanar

TABLE I. Structural parameters, energies, and harmonic frequencies of various isomers calculated with B3LYP/aug-cc-pVTZ.

C ₅ ISOMERS	Sym.	E _R (eV)	Rotational constants (MHz)	μ (Debyes)	Harmonic fundamentals (cm ⁻¹)
	<i>l</i> -C ₅ X ¹ Σ _g ⁺	0.0 ^a	B=2570.4 MHz	0.0	2039(σ _g), 797(σ _g), 2249(σ _u), 1494(σ _u) 224(π _g), 563(π _u), 119(π _u)
	<i>c</i> -C ₅ X ¹ A ₁	2.6	A=3852. B=5182.5 C=4567.9	0.9276	1805(A ₁), 1415(A ₁) 1101(A ₁), 791(A ₁) 546(B ₁), 239(B ₁) 908(B ₂), 381(B ₂) 175(B ₂)
	<i>t</i> -C ₅ X ¹ A ₁	3.3	A=1589.50 B=5592.3 C=4136.9	0.4173	1848(A ₁), 1059(A ₁) 723(A ₁), 940(A ₁) 271(B ₁), 1619(B ₂) 800(B ₂), 251(B ₂) 348(A ₂)
	<i>p</i> -C ₅ X ¹ A ₁ '	4.4	A=1112 B=1112 C=1023.4	0.0	1236(A ₁ '), 808(A ₂ '') 706(A ₁ '), 1007(E') 583(E') 425(E'')

^aE(B3LYP/aug-cc-pVTZ)=-190.272915 a.u.; TD-UB3LYP triplet state relative energies: 2.6 eV (*l*-C₅), 4.1 eV (*c*-C₅), 4.5 eV (*t*-C₅), and 6.5 eV (*p*-C₅).

geometry of *D*_{3h} symmetry, *p*-C₅. They lie 60, 76, and 102 kcal/mol over the linear form, respectively. To confirm the singlet state character of the ground state, X¹Σ_g⁺(*l*-C₅), X¹A₁(*c*-C₅), X¹A₁(*b*-C₅), and X¹A₁'(*p*-C₅), we have evaluated, with TD-UB3LYP, the vertical energies to the first triplet electronic states. These excitations are equal to 2.6 eV(*l*-C₅), 4.1 eV(*c*-C₅), 4.5 eV(*t*-C₅), and 6.5 eV(*p*-C₅). The energy difference between the two most stable isomers, *l*-C₅ and *c*-C₅, is of the same order of magnitude as the excitation to the lowest triplet state.

The molecular structure of *l*-C₅

Considering the large energy differences, the only isomer that is relevant from the point of view of astrophysical detection is the linear X¹Σ_g⁺. Remaining isomers can possibly be important as chemical intermediates and therefore relevant in discussions of chemical reaction mechanisms. Thus, the high level *ab initio* calculations of spectroscopic properties can be focused on the linear structure. Preliminary results and the vertical excitation energies obtained here verify that the separation of electronic states is large enough for neglecting rovibronic effects in the analysis of the IR spectrum.

Static correlation plays an important job in C₅. For the equilibrium geometry, the statistical weight of the Hartree-Fock determinant in the CASSCF wave function is lower than the 80%. Furthermore, as C₅ is a chemical species of low stability, the HF contribution decreases significantly in regions of the potential energy surface needed for the force field computation. For this reason, the CASSCF/CASPT2 method,^{8,37} represents a good and efficient choice for the spectroscopic characterization of C₅.

Test calculations with different active spaces have been performed for evaluating the weight of electronic configuration in the ground electronic state wave function. The definitive results (see Tables II, III, and V) were performed with two basis sets ANO-L type (3s2p1d and 4s3p2d1f) (Ref. 38) and an active space comprising 12 electrons in 12 orbitals (12in12); four valence orbitals were left inactive (and the core orbitals) and four were moved to the virtual space.

In Table II, the CASPT2 structural parameters of *l*-C₅ computed with the geometry optimization algorithm implemented in MOLCAS are detailed and compared with the ones determined minimizing the potential energy surface calculated from a grid of energies. With the largest basis set, ANO-L 4s3p2d1f, the *inner* internuclear distances, R₁ and R₂, have been calculated to be 1.279 Å, whereas the two *outer* distances, R₃ and R₄, to be 1.291 Å (see Fig. 1). This leads to a rotational constants equal to B_e=0.085 239 cm⁻¹, which compares very well with the experimental data of 0.085 313 3 cm⁻¹ determined with diode laser spectroscopy in gas phase.¹⁷

In Table II, the calculated distances are also compared with MP4/6-31G(d), CEPA-I/150 CGTOs, MP2/6-31G*, CCSD+T+FOCOs/TZP, CCSD(T)/275 CGTOs, CCSD(T)/cc-pVDZ, previous *ab initio* calculations, and density functional theory.^{15,26-32} The CASPT2 distances are slightly shorter than those obtained with coupled-cluster methods.

The electronic spectrum of *l*-C₅

The electronic spectrum of *l*-C₅ has been investigated with CASPT2/ANO-L calculations applied over the active space containing 12 orbitals. Table III shows the lowest

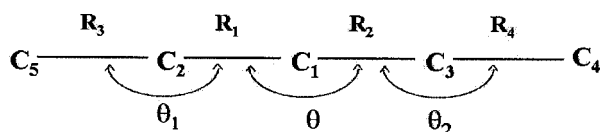
TABLE II. CASPT2/ANO-L structural parameters (in Å) and rotational constant (in cm^{-1}) corresponding to the minimum energy geometry of singlet ground state of $l\text{-C}_5$.

	ANO-L ^a (4s3p2d1f)	ANO-L ^b (3s2p1d)		Previous calc.
R_1+R_2 (inner)	1.279	1.300 2	1.275 ^c	MP4/6-31G(d)
			1.283 ^d	CEPA-1/150 CGTOs
			1.291 ^e	MP2/6-31G(d)
			1.287 ^f	CCSD+T+FOCOs/TZP
			1.2819 ^g	CCSD(T)/275 cGTOs
			1.3057 ^h	CCSD(T)/cc-pVDZ
			1.290 ⁱ	DFT
$R_3=R_4$ (outer)	1.290 9	1.316 2	1.271 ^c	MP4/6-31G(d)
			1.289 ^d	CEPA-1/150 CGTOs
			1300 ^e	MP2/6-31G(d)
			1.294 ^f	CCSD+T+FOCOs/TZP
			1.2896 ^g	CCSD(T)/275 cGTOs
			1.3164 ^h	CCSD(T)/cc-pVDZ
			1.299 ⁱ	DFT
B_e	0.085 239	0.082 291	B_0 (expt.)	0.085 313 3 ^j

^aReference geometry for the fit.^bCalculated minimizing the fitted potential energy surface.^cReference 15.^dReference 26.^eReferences 27 and 29.^fReference 28.^gReference 31.^hReference 32.ⁱReference 30.^jReference 17.

energy states classified by symmetries, the excitation energies calculated from the minimum of the singlet ground electronic state, and the corresponding main configuration. Energies are compared with the few available experimental data, taken from Ref. 23. Furthermore, the CASPT2 excitation energies are compared with the MRDCI calculations of Pachioni and Koutecky²⁵ and the MRDCI+Q values of Kolbuszewski.²⁴ The authors of Ref. 25 have employed a double zeta basis set with polarization functions that have been extended using diffuse functions in their second work.²⁴

Two sets of excitation energies are shown in Table III for each electronic state. The data in first column are vertical energies, whereas the second column data are adiabatic energies. These last levels have been computed optimizing the geometry of the excited state with a single restriction: the linearity of the molecule has been imposed. As was expected, the lowest excitations correspond to degenerate triplet Π states, lying 1.74 eV($1^3\Pi_g$), 1.85 eV($1^3\Pi_u$), and 2.05 eV($1^3\Sigma_u^+$) over the ground electronic state. The lowest singlet excited states are located at 2.34 eV over the minimum, which is high enough that there should not be any

FIG. 1. The C_5 cluster and the internal independent coordinates.

appreciable vibronic contribution to the ground state vibrations. With few exceptions, it may be inferred that the effect of the geometry optimization on the excitations is very small.

The few available experimental data concerning electronic transitions of carbon chains come from Maier *et al.*²² Given the lack of available experimental data for comparing our results, we focus our attention on two bands of the electronic absorption spectra trapped in 5 K neon matrices. The origins appear at 230 nm (6.4 eV) and 510 nm (2.43 eV), respectively, and have been assigned to the $^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ and the $^1\Pi_u \leftarrow X^1\Sigma_g^+$ transitions on the basis of previous MRCI calculations that placed them at 6.76 and 3.18 eV (Ref. 25) and 6.35 and 2.89 eV.²⁴ It is evident that the enlargement of the basis set causes a better agreement with the experimental values. Our calculations place the $^1\Pi_u \leftarrow X^1\Sigma_g^+$ transition at 2.61 eV (vertical excitation) and 2.58 eV (adiabatic energy) closer to the weaker band observed at 2.43 eV (Ref. 22) than the previous calculations. The $^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ transition is computed to be at 7.02 eV (vertical excitation) and 6.65 eV (adiabatic energy) closer to the electronic absorption band observed at 6.40 eV.²² The optimization of the geometry of the excited electronic state improves the results by 0.03 eV. Perturbative CASPT2 method appears to be more efficient than MRCI for the interpretation of electronic spectra.

In the case of the $^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ transition, CASPT2 calculations predict energies of 7.02 eV (vertical excitation) and 6.65 eV (adiabatic energy). The optimization of the geometry leads to a significant improvement for the theoretical

TABLE III. Vertical excitation energies and excitation adiabatic energies (in eV) of *l*-C₅ calculated with CASPT2 and ANO-L 4s3p2d1f basis set. $E_{\min} = -189.829\,308$ hartree.

Symmetry	Vertical excitation energies (eV)	Adiabatic energies (eV)	Expt. ^a	Previous calc. ^b	Main configuration
$1^1\Sigma_g^+$	0	0		0	$(1\pi_u)^4(6\sigma_g)^2(5\sigma_u)^2(1\pi_g)^4$
$3^1\Pi_g$	1.79	1.74		2.03	$(1\pi_u)^4(6\sigma_g)^2(5\sigma_u)^1(1\pi_g)^4(2\pi_u)^1$
$3^1\Pi_u$	1.86	1.84		1.96	$(1\pi_u)^4(6\sigma_g)^1(5\sigma_u)^2(1\pi_g)^4(2\pi_u)^1$
$3^1\Sigma_u^+$	2.23	2.05		2.21	$(1\pi_u)^4(6\sigma_g)^2(5\sigma_u)^2(1\pi_g)^3(2\pi_u)^1$
$1^1\Sigma_u^-$	2.43	2.33		2.62	$(1\pi_u)^4(6\sigma_g)^2(5\sigma_u)^2(1\pi_g)^3(2\pi_u)^1$
$1^1\Delta_u$	2.4	2.34		2.55	$(1\pi_u)^4(6\sigma_g)^2(5\sigma_u)^2(1\pi_g)^3(2\pi_u)^1$
$3^1\Delta_u$	2.43	2.37		2.41	$(1\pi_u)^4(6\sigma_g)^2(5\sigma_u)^2(1\pi_g)^3(2\pi_u)^1$
$3^1\Sigma_u^-$	2.47	2.39		2.52	$(1\pi_u)^4(6\sigma_g)^2(5\sigma_u)^2(1\pi_g)^3(2\pi_u)^1$
$1^1\Pi_g$	2.54	2.51		2.81	$(1\pi_u)^4(6\sigma_g)^2(5\sigma_u)^1(1\pi_g)^4(2\pi_u)^1$
$1^1\Pi_u$	2.61	2.58	2.43	2.89	$(1\pi_u)^4(6\sigma_g)^1(5\sigma_u)^2(1\pi_g)^4(2\pi_u)^1$
$5^1\Sigma_u^-$	2.83	2.76			$(1\pi_u)^4(6\sigma_g)^1(5\sigma_u)^1(1\pi_g)^4(2\pi_u)^2$
$5^1\Pi_u$	3.66	3.64			$(1\pi_u)^4(6\sigma_g)^2(5\sigma_u)^1(1\pi_g)^3(2\pi_u)^2$
$5^1\Pi_g$	3.72	3.7			$(1\pi_u)^4(6\sigma_g)^1(5\sigma_u)^2(1\pi_g)^3(2\pi_u)^2$
$3^1\Sigma_g^+$	4.3	4.11		4.24	$(1\pi_u)^3(6\sigma_g)^2(5\sigma_u)^2(1\pi_g)^4(2\pi_u)^1$
$3^1\Delta_g$	4.56	4.47		4.45	$(1\pi_u)^3(6\sigma_g)^2(5\sigma_u)^2(1\pi_g)^4(2\pi_u)^1$
$5^1\Sigma_g^+$	4.6	4.31			$(1\pi_u)^4(6\sigma_g)^2(5\sigma_u)^2(1\pi_g)^2(2\pi_u)^2$
$3^1\Sigma_g^-$	4.7	4.49			$(1\pi_u)^3(6\sigma_g)^2(5\sigma_u)^2(1\pi_g)^4(2\pi_u)^1$
$1^1\Sigma_g^-$	4.9	4.72		4.50	$(1\pi_u)^3(6\sigma_g)^2(5\sigma_u)^2(1\pi_g)^4(2\pi_u)^1$
$1^1\Delta_g$	4.67	4.50		4.48	$(1\pi_u)^3(6\sigma_g)^2(5\sigma_u)^2(1\pi_g)^4(2\pi_u)^1$
$5^1\Delta_g$	5.87	5.69			$(1\pi_u)^4(6\sigma_g)^1(5\sigma_u)^1(1\pi_g)^3(2\pi_u)^3$
$5^1\Delta_u$	6.47	6.06			$(1\pi_u)^3(6\sigma_g)^1(5\sigma_u)^1(1\pi_g)^3(2\pi_u)^2$
$1^1\Sigma_u^+$	7.02	6.65	6.40	6.35	$(1\pi_u)^4(6\sigma_g)^2(5\sigma_u)^2(1\pi_g)^3(2\pi_u)^1$

^aReference 24.^bReference 25.

prediction that is in a very good agreement with the observations (6.40 eV). The excitation here results in an appreciable change in the molecular geometry.

The infrared spectrum of C₅

Theoretical results are here of utmost importance. We focus our attention on two groups of infrared active vibrations: the asymmetric stretching modes, which were responsible for the first detection of the molecule, and the degenerate π_u modes lying in the far infrared region. An accurate prediction of the band centers requires the inclusion of anharmonicity effects in the models because, as was observed for C₃,³ neutral carbon chains can be really floppy molecules. Later on, we discuss the importance of the effect of anharmonicity, a question that has generated great interest.

The spectroscopic parameters have been calculated with classical perturbation theory after producing a CASPT2/ANO-L (3s2p1d) anharmonic force field. The method represents an efficient procedure given the number of independent variables and the multiconfigurational behavior of the molecule. Thus, the force field has been computed from the determination of a local full-dimensional potential energy surface defined as functions of linear combination of the internal coordinates (see Fig. 1). A grid of 1350 geometries around a reference structure shown in Table II has been selected taking symmetry and energy criteria into consideration. The stretching coordinates have been allowed to change by 0.15 Å, the two external angles, θ_1 and θ_2 , by 6°,

and the angle θ by 5°. The analytic expression of the PES that contains four degree coupling terms is a well known product of Taylor series:

$$\begin{aligned}
 V(q_1, q_2, \dots, q_r) = & \sum_{i=1}^{10} \sum_{j=i}^{10} \frac{1}{2} f_{ij} q_i q_j \\
 & + \sum_{i=1}^{10} \sum_{j=i}^{10} \sum_{k=j}^{10} \frac{1}{6} f_{ijk} q_i q_j q_k \\
 & + \sum_{i=1}^{10} \sum_{j=i}^{10} \sum_{k=j}^{10} \sum_{l=k}^{10} \frac{1}{24} f_{ijkl} q_i q_j q_l q_k,
 \end{aligned}$$

where $q_m = S_m - S_m^{\text{REF}}$ represents simple linear combinations of the internal coordinates defined in Fig. 1. Symmetry coordinates are defined by the following equations:

$$S_1 = \frac{1}{\sqrt{2}}(R_1 + R_2), \quad S_2 = \frac{1}{\sqrt{2}}(R_3 + R_4),$$

$$S_3' = \frac{1}{\sqrt{2}}(R_1 - R_2), \quad S_4 = \frac{1}{\sqrt{2}}(R_3 - R_4),$$

$$S_i^{x,s} = \frac{1}{\sqrt{2}}(\theta_1^{x,s} + \theta_2^{x,s}), \quad (i,s) = (5,x), (6,y),$$

TABLE IV. Anharmonic force field for the ground electronic state of $I-C_5$ calculated with CASPT2/ANO-L. Force field in at. J, distances in Å, and angles in deg.

f_{ij}		f_{ijkl}	
f_{22}	9.854	f_{1111}	-134.007
f_{33}	10.218	f_{2222}	197.283
f_{44}	9.871	f_{3333}	187.465
f_{55}	0.119	f_{4444}	268.734
f_{66}	0.119	f_{5555}	-0.685
f_{77}	0.194	f_{6666}	-0.685
f_{88}	0.194	f_{7777}	1.320
f_{99}	0.194	f_{8888}	1.320
f_{1010}	0.194	f_{9999}	1.320
f_{21}	-0.246	$f_{10101010}$	1.320
f_{43}	0.657	f_{2211}	-35.356
		f_{3311}	170.954
		f_{3322}	-3.761
		f_{4411}	17.680
		f_{4422}	172.756
		f_{5511}	77.869
		f_{5522}	-32.714
		f_{5533}	5.252
		f_{5544}	-4.061
		f_{6611}	77.869
		f_{6622}	-32.714
		f_{6633}	5.252
		f_{6644}	-4.061
		f_{7711}	4.561
		f_{7722}	-10.461
		f_{7733}	-2.249
		f_{7744}	-5.193
		f_{8811}	4.561
		f_{8822}	-10.461
		f_{8833}	-2.249
		f_{8844}	-5.193
		f_{9911}	4.561
		f_{9922}	-10.461
		f_{9933}	-2.249
		f_{9944}	-5.193
		f_{101011}	4.561
		f_{101022}	-10.461
		f_{101033}	-2.249
		f_{101044}	-5.193
		f_{1112}	-135.263
		f_{2221}	5.820
		f_{3334}	1.452
		f_{4443}	18.880
		f_{1143}	9.105
		f_{2243}	1.392
		f_{5521}	14.875
		f_{6621}	14.875
		f_{7721}	-4.654
		f_{8821}	-4.654
		f_{9921}	-4.654
		f_{101021}	-4.654
		f_{4321}	-0.324

$$S_i^{xs} = \frac{1}{\sqrt{3}}(\theta_2^{xs} - \theta_1^{xs} + \theta^{xs}), \quad (i,s) = (7,x), (8,y),$$

$$S_i^{xs} = \frac{1}{\sqrt{3}}(\theta_2^{xs} - \theta_1^{xs} - \theta^{xs}), \quad (i,s) = (9,x), (10,y).$$

Table IV shows the anharmonic force field and Table V the anharmonic spectroscopic parameters calculated with the FIT-ESPEC code.³⁹ The harmonic fundamentals are compared with previous calculations, whereas the observable parameters (band centers) are compared with available experimen-

TABLE V. Spectroscopic parameters for the ground electronic state of *I*-C₅ calculated with the CASPT2 anharmonic force field.

	Calc. (present work)		Previous calc.			
$\omega_1(\sigma_g)$ (cm ⁻¹)	1962	2220 ^a	2018 ^b	2010 ^c	2008 ^d	1967 ^e
$\omega_2(\sigma_g)$ (cm ⁻¹)	750	863 ^a	786 ^b	790 ^c	786 ^d	770 ^e
$\omega_3(\sigma_u)$ (cm ⁻¹)	2210	2344 ^a	2358 ^b	2168 ^c	2212 ^d	
$\omega_4(\sigma_u)$ (cm ⁻¹)	1433	1632 ^a	1471 ^b	1477 ^c	1436 ^d	
$\omega_5(\pi_g)$ (cm ⁻¹)	221	222 ^a	281 ^b			
$\omega_6(\pi_u)$ (cm ⁻¹)	452	648 ^a	487 ^b			
$\omega_7(\pi_u)$ (cm ⁻¹)	106	112 ^a	130 ^b			
	Calc. (present work)		Expt.	Scaling force field ^c		
$\nu_1(\sigma_g)$ (cm ⁻¹)	1910					2008
$\nu_2(\sigma_g)$ (cm ⁻¹)	817	775.8 ^f	798±45 ^g	779 ^h		792
$\nu_3(\sigma_u)$ (cm ⁻¹)	2189	2169.442 05 ⁱ	2169.4404 ^j	2164 ^k		2169
		2157.0 ^f	2169.4410 ^l			
$\nu_4(\sigma_u)$ (cm ⁻¹)	1422	1446.6 ^m	1443.2 ^f			1478
$\nu_5(\pi_g)$ (cm ⁻¹)	218	216 ^h	218±13 ^l			209
$\nu_6(\pi_u)$ (cm ⁻¹)	447	535 ^h				570
$\nu_7(\pi_u)$ (cm ⁻¹)	102	102 ⁿ	118±13 ^l	106 ^h		119
2 ν_1 (cm ⁻¹)	3811					4005
2 ν_2 (cm ⁻¹)	1625					1548
2 ν_3 (cm ⁻¹)	4366		4327.8 ^f			
2 ν_4 (cm ⁻¹)	2845					2952
2 ν_5 (cm ⁻¹)	350		444 ^g			
2 ν_6 (cm ⁻¹)	927		1024 ^g			
2 ν_7 (cm ⁻¹)	203		202 ^g			
$\nu_2 + \nu_3$ (cm ⁻¹)	2999		2939.9 ^f			2955
B_0 (MHz)	2485.8			2557.63 ^l		
D_0 (kHz)	0.118			0.161 ^l		
$B_{v_3=1}$ (MHz)	2472.3			2545.040 ^l		
q_5 (MHz)	1.05			2.36 ^l		
q_7 (MHz)	3.93			3.99 ^l		

^aHF/6-31G(d) (Ref. 15).^bMP2/6-31G(d) (Refs. 27 and 29).^cCEPA-1/150cGTOs (Ref. 26).^dCCSD(T)/275 cGTOs (Ref. 31).^eCCSD(T)/cc-pVDZ (Ref. 32).^fIR (Kr matrix) (Ref. 19).^gAnion photoelectron spectroscopy (Ref. 20).^hAnion photodetachment spectroscopy (Ref. 21).ⁱAstrophysical observation (IR) (Ref. 3).^jDiode laser absorption spectroscopy (Ref. 11).^kIR (Ar matrix) (Ref. 12).^lDiode laser absorption spectroscopy (gas phase) (Ref. 17).^mIR (Ar matrix) (Ref. 18).ⁿAstrophysical observation (FIR) (Ref. 5).

tal data. We also provide the calculated overtones, some combination bands, and the relevant spectroscopic parameters.

An algorithm implemented in FIT-ESPEC makes it possible to obtain the minimum energy geometry corresponding to the fitted potential energy surface. The corresponding structural data are shown in Table II ($R_1=R_2=1.302$ Å and $R_3=R_4=1.316$ Å), whereas the rotational constant B_0 is shown in Table VI. It has been evaluated to be 2467 MHz (=0.082 291 cm⁻¹). We notice the slightly longer bond lengths, which are due to the use of the smaller ANO-L basis set in the generation of the energy surface.

The better known mode, the $\nu_3(\sigma_u)$ antisymmetric

stretching, shows that the computed force field is accurate enough to reproduce observations. Its fundamental has calculated to be 2189 cm⁻¹, in a good agreement with the experimental values obtained in gas phase with diode laser spectroscopy [2169.44 cm⁻¹ (Refs. 11 and 17)]. Infrared measurements in Ar matrix or Kr matrices yield band located at 2164 cm⁻¹ (Ref. 12) and 2157 cm⁻¹,¹⁹ respectively. First astrophysical observations provide a band located at 2169.44 cm⁻¹.³ Our model also confirms the bands observed by Szczepanski *et al.*¹⁹ in a Kr matrix at 4327.8 and 2939.9 cm⁻¹ that they tentatively assigned to the 2 ν_3 overtone and to the $\nu_2 + \nu_3$ combination bands. Here, they have been computed to be 4366 and 2999 cm⁻¹ from the CASPT2

TABLE VI. Band centers (in cm^{-1}), rotational constants (in MHz), and fundamental band IR intensities (I in $\text{D}^2/\text{\AA}^2 \text{amu}$) of various isotopomers of C_5 calculated with CASPT2/ANO-L.

	C-C-C-C-C	C-C-C-C- ^{13}C	^{13}C -C-C-C- ^{13}C	C-C-C- ^{13}C - ^{13}C
$\nu_1(\sigma_g)$	1910	1910	1903	1879
$\nu_2(\sigma_g)$	817	816	806	809
$\nu_3(\sigma_u)$	2189 ($I=4054$)	2159 ($I=4025$)	2149 ($I=4054$)	2091 ($I=3999$)
$\nu_4(\sigma_u)$	1422 ($I=100$)	1403 ($I=105$)	1389 ($I=73$)	1400 ($I=110$)
$\nu_5(\pi_g)$	218	218	217	214
$\nu_6(\pi_u)$	447 ($I=7$)	440 ($I=7$)	439 ($I=7$)	435 ($I=7$)
$\nu_7(\pi_u)$	102 ($I=11$)	100 ($I=11$)	99 ($I=11$)	100 ($I=11$)
$2\nu_3$	4366	4304	4285	4170
$\nu_2 + \nu_3$	2999	2972	2946	2850
B_0	2489	2486	2406	2465
$B\nu_3=1$	2472	2472	2394	2452

force field. As the assignments of Ref. 19 are based on the isotopic substitution effect that has not been measured, we provide in Table VI predicted values for several isotopomers.

To our knowledge, the fundamental $\nu_1(\sigma_g)$ calculated at 1910 cm^{-1} has not been observed. For the remaining stretching fundamentals, our calculations [$\nu_2(\sigma_g)=817 \text{ cm}^{-1}$ and $\nu_4(\sigma_u)=1422 \text{ cm}^{-1}$] are also in a good agreement with the experimental data that vary from 775 to 779 cm^{-1} for $\nu_2(\sigma_g)$ (Refs. 19–21) and from 1443 to 1447 cm^{-1} for $\nu_4(\sigma_u)$ (IR measured in Ar and Kr matrices.^{18,19}). There are no available measurements performed in gas phase.

The $\nu_5(\pi_g)$ and the $\nu_7(\pi_u)$ fundamentals have been predicted to lie 218 ± 13 and $118 \pm 3 \text{ cm}^{-1}$ from the l -type doubling constants q_5 and q_7 obtained using infrared diode laser spectroscopy.¹⁷ Our calculated $\nu_5(\pi_g)$ fundamental, 218 cm^{-1} , also confirms the assignment for the symmetric bending. For the very low frequency bending mode, predictions from experiments are not accurate enough, although previous *ab initio* calculations performed within the harmonic approximation placed it between 112 and 130 cm^{-1} .^{15,27,29} It has been calculated to be 119 cm^{-1} from the scaling force field of Ref. 26.

However, the $\nu_7(\pi_u)$ fundamental is the transition of largest interest for DAMIR since its determination allows the discussion of the previous astrophysical observations performed with the far infrared (FIR) telescope³ and helps future measurements in sources where the abundance of C_5 is expected to be very low. Our computations including anharmonicities place the band center around 102 cm^{-1} , which is in a good agreement with the band center that has been observed at 102 cm^{-1} with the ISO. The overtone calculated to be 203 cm^{-1} is also in a good agreement with the laboratory measurement of 202 cm^{-1} (Ref. 20) arising from photodetachment spectroscopy which also confirms the assignment. The CASPT2 $\nu_7(\pi_u)$ anharmonic fundamental (at 102 cm^{-1}) validates the assignment to C_5 of the band observed at 102 cm^{-1} with the ISO telescope.

Anharmonic constant x_{77} has been found to be 0.076 cm^{-1} . The difference $2(\nu_7)-(2\nu_7)=2 \text{ cm}^{-1}$ shows that C_5 is a relatively rigid molecule. The shape of the restricted potential for the asymmetric bending approaches that of a harmonic vibration.

Table VI provides the spectroscopic parameters of various isotopomers of C_5 calculated using perturbation theory from the force field. Isotopomers have been selected in the way that few atoms corresponding to the most abundant isotope ^{12}C are substituted by ^{13}C (relative abundance $\propto 1/45$). Isotopic substitution can produce displacements of 30 cm^{-1} in the case of the stretching modes and small variations in the far infrared region. ν_7 varies from 102 cm^{-1} in $^{12}\text{C}-^{12}\text{C}-^{12}\text{C}-^{12}\text{C}$ to 99 cm^{-1} in $^{13}\text{C}-^{12}\text{C}-^{12}\text{C}-^{13}\text{C}$. Isotopic shifts can be only compared with the ones obtained from the scaling force field of Ref. 26.

CONCLUSIONS

CASPT2/ANO-L calculations have been performed for predicting vertical and adiabatic electronic transitions and vibrational spectroscopic parameters for the most stable linear isomer of C_5 . The infrared spectra of various isotopomers are analyzed using an anharmonic force field that includes four coupling terms.

The highly correlated force field appears to be efficient for the determination of the anharmonic fundamentals and the rotational constants, allowing a discussion of previous assignments of experimental measures and previous tentative astrophysical observations. For example, the band centers of the fundamental and overtone of the IR active stretching $\nu_3(\sigma_u)$ have been calculated to be at 2189 and 4366 cm^{-1} , which confirm previous assignments. The $\nu_7(\pi_u)$ fundamental has been calculated at 102 cm^{-1} , which validates the assignment to C_5 of the band observed at 102 cm^{-1} with the ISO telescope.

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¹A. E. Douglas, *Nature (London)* **269**, 130 (1977).

²J. Cernicharo, J. R. Goicoechea, and E. Caux, *Astrophys. J.* **534**, L199 (2000).

³P. F. Bernath, K. H. Hinkle, and J. J. Keady, *Science* **244**, 562 (1989).

⁴R. Terziya and E. Herbst, *Astrophys. J.* **501**, 207 (1998).

⁵J. Goicoechea, J. Cernicharo, H. Massó, and M. L. Senent, *Astrophys. J.* **609**, 225 (2004).

⁶H. Massó, M. L. Senent, P. Rosmus, and M. Hochlaf, *J. Chem. Phys.* **124**, 234304 (2006).

⁷M. L. Senent, H. Massó, and M. Hochlaf (unpublished).

⁸K. Andersson, P.-Å. Malmqvist, B. O. Roos, A. J. Sadlej, and K. Wolinski, *J. Phys. Chem.* **94**, 5483 (1990); K. Andersson, P.-Å. Malmqvist, and B. O. Roos, *J. Chem. Phys.* **96**, 1218 (1992).

⁹G. Karlström, R. Lindh, P.-Å. Malmqvist *et al.*, MOLCAS, Version 6.4; *Comput. Mater. Sci.* **28**, 222 (2003).

- ¹⁰A. Van Orden and R. J. Saykally, *Chem. Rev.* (Washington, D.C.) **98**, 2313 (1998).
- ¹¹J. R. Heath, A. L. Cooksy, M. H. W. Gruebele, C. A. Schmuttenmaer, and R. J. Saykally, *Science* **244**, 564 (1989).
- ¹²M. Vala, T. M. Chandrasekhar, J. Szczepanski, R. J. Van Zee, and W. Weltner, Jr., *J. Chem. Phys.* **90**, 595 (1989).
- ¹³K. R. Thompson, R. L. DeKock, and W. Weltner, Jr., *J. Am. Chem. Soc.* **93**, 4688 (1971).
- ¹⁴W. R. M. Graham, K. I. Dismuke, and W. Weltner, Jr., *Astrophys. J.* **204**, 301 (1976).
- ¹⁵K. Raghavachari and J. S. Binkley, *J. Chem. Phys.* **87**, 2191 (1987).
- ¹⁶N. Moazzen-Ahmadi, A. R. W. McKellar, and T. Amano, *Chem. Phys. Lett.* **157**, 1 (1989).
- ¹⁷N. Moazzen-Ahmadi, A. R. W. McKellar, and T. Amano, *J. Chem. Phys.* **91**, 2140 (1989).
- ¹⁸R. H. Kranze and W. R. M. Graham, *J. Chem. Phys.* **96**, 2517 (1992).
- ¹⁹J. Szczepanski, S. Ekern, C. Chapo, and M. Vala, *Chem. Phys.* **211**, 359 (1996).
- ²⁰D. W. Arnold, S. E. Bradforth, T. N. Kitsopoulos, and D. M. Neumark, *J. Chem. Phys.* **95**, 8753 (1991).
- ²¹T. N. Kitsopoulos, C. J. Chick, Y. Zhao, and D. M. Neumark, *J. Chem. Phys.* **95**, 5479 (1991).
- ²²J. P. Maier, G. H. A. Walker, and D. A. Bohlender, *Astrophys. J.* **602**, 286 (2004).
- ²³D. Forney, P. Freivogel, M. Grutter, and J. P. Maier, *J. Chem. Phys.* **104**, 4954 (1996).
- ²⁴M. Kolbuszewski, *J. Chem. Phys.* **102**, 3679 (1995).
- ²⁵G. Pachionni and J. Koutecky, *J. Chem. Phys.* **88**, 1066 (1988).
- ²⁶P. Botschwina and P. Sebald, *Chem. Phys. Lett.* **160**, 485 (1989).
- ²⁷J. M. L. Martin, J. P. Francois, and R. Gijbels, *J. Chem. Phys.* **90**, 3403 (1989); *J. Comput. Chem.* **12**, 52 (1991).
- ²⁸J. Kurtz and L. Adamowicz, *Chem. Phys. Lett.* **162**, 342 (1989).
- ²⁹J. Kurtz and L. Adamowicz, *Astrophys. J.* **370**, 784 (1991).
- ³⁰J. Hutter, H. P. Lüthi, and F. Diederich, *J. Am. Chem. Soc.* **116**, 750 (1994).
- ³¹P. Botschwina, *J. Chem. Phys.* **101**, 853 (1994).
- ³²J. M. L. Martin and P. R. Taylor, *J. Chem. Phys.* **100**, 6047 (1996).
- ³³M. S. Deleuze, M. G. Giuffreda, J. P. François, and L. S. Cederbaum, *J. Chem. Phys.* **111**, 5851 (1999).
- ³⁴Z. Cao, S. D. Peyerimhoff, F. Grein, and Q. Zhang, *J. Chem. Phys.* **115**, 2062 (2001).
- ³⁵P. Fuentealba, *Phys. Rev. A* **58**, 4232 (1998).
- ³⁶M. Bianchetti, P. F. Buonsante, F. Ginelli, H. E. Roman, R. A. Broglia, and F. Alasia, *Phys. Rep.* **357**, 459 (2002).
- ³⁷B. O. Roos, P. R. Taylor, and P. E. M. Siegbahn, *Chem. Phys.* **48**, 157 (1980); B. O. Roos, in *Ab Initio Methods in Quantum Chemistry*, Advances in Chemical Physics, edited by K. P. Lawley (Wiley, Chichester, England, 1987), Pt. II, Chap. 69, p. 399.
- ³⁸P.-O. Widmark, P.-A. Malmqvist, and B. O. Roos, *Theor. Chim. Acta* **77**, 291 (1990).
- ³⁹M. L. Senent, FIT-ESPEC, a Fortran code for calculating spectroscopic parameters from a force field in internal coordinates, 2007.