ANHARMONIC SPECTROSCOPIC STUDY OF THE GROUND ELECTRONIC STATE OF VARIOUS C₄ RADICAL ISOTOPOMERS

M. L. SENENT,¹ H. MASSÓ,¹ AND M. HOCHLAF²

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ABSTRACT

Quartic force fields for the ground electronic states of the most stable C₄ radical isomers [l-C₄(X³Σ_g[−]) and r-C₄(X¹A_g)] are computed at the same level of theory. These computations are performed using interaction configuration ab initio methods and the cc-pVTZ basis set. These force fields on symmetry-adapted coordinates are derived from full six-dimensional potential energy surfaces generated close to their equilibrium geometries. For both isomers, sets of spectroscopic parameters of the most abundant isotopic varieties are determined with perturbation theory. This includes rotational constants, harmonic wavenumbers, anharmonic wavenumbers for the fundamentals, and some overtones, combination modes, and l-doubling terms. Finally, our results are compared with experimental data measured with different techniques that allow us to discuss assignments of previous astrophysical observations. Specifically, we are focusing in predicting frequencies for the low bendings allowing understanding patterns detected with far-infrared techniques.

Subject headings: astrochemistry — infrared: ISM — ISM: molecules — molecular data

1. INTRODUCTION

During the last decade, tetracarbon has been one of the chemical species that has attracted major interest for the astrophysics community, since it is expected to be among the small C_n radicals present in carbon-rich sources (Cernicharo et al. 2000). Small C_n chains can be important intermediates for chemical reactions in the gas phase, and they had been related to the observed diffuse interstellar bands (Douglas 1977).

Consequently, the search for carbon chains in interstellar sources is so frequent. The presence of small carbon clusters such as C₃ (Cernicharo et al. 2000) suggests the existence in the same sources of other compounds of similar chemical properties. Recently, the astrophysicists of DAMIR (Cernicharo et al. 2002) have observed in Sgr B2, IRC +10216, CRL 2688, CRL 618, and NGC 7027 a pattern of bands at 57 μm (174 cm^{−1}) with the *Infrared Space Observatory* unspecified in the database. It consists of a complex feature with four subcomponents at 57.0, 57.6, 57.9, and 58.2 μm, which cannot be identified to any far-infrared spectra of the most abundant carbon chains, for instance, C₃, C₅. Several other experimentally well-characterized molecular candidates presenting low bending modes lying in the 160–220 cm^{−1} energy range were checked without success. Instead, the antisymmetric deformations of the C₄H and C₄ radicals were proposed. However, very few data are available in the literature for these two molecules, especially for C₄. The low chemical stability of this radical made the development of experiments in the laboratory for its investigation by classical techniques difficult. Many of its properties must be deduced using theoretical predictions. A definitive assignment of the astrophysical band implies collecting new spectroscopic parameters in the database for astrophysics.

Previous experimental works dealing with this and other small C_n terms were summarized in the review of Van Order & Saykally (1998). It turns out from this review the paucity of data relative to C₄ and that many aspects involving its spectroscopic properties are misinterpreted. Briefly, the infrared (IR) spectrum of l-C₄

trapped in Ar matrix by Shen & Graham (1989) and the gas-phase IR spectrum of l-C₄ by Heath & Saykally (1991) have identified the antisymmetric CC stretching ν₃ fundamental at 1543.4 cm^{−1} in matrix and at 1548.9 cm^{−1} in the gas phase. Later studies performed in the Ne matrix (Smith et al. 1994), in solid neon (Forney et al. 1995), and in Ne, ortho-D₂, and para-H₂ matrices (Tam et al. 1997) placed the origin ν₃ band at 1547 cm^{−1}, whereas the cooled Kr matrix C₄ isolation study of Szczepanski et al. (1996) has located it at lower energies (1539 cm^{−1}). The situation is, however, rather critical for the other modes which are known with relatively large error bars, making the unequivocal assignment of some interstellar bands difficult. Indeed, the gas-phase symmetric stretching (ν₁) and the trans-bending (ν₄) fundamentals have been determined by photoelectron spectroscopy to be 2032 ± 50 cm^{−1} (Arnold et al. 1991) and 2057 ± 50 cm^{−1} (Xu et al. 1997) and 339 ± 55 cm^{−1} (Arnold et al. 1991) and 323 ± 50 cm^{−1} (Xu et al. 1997), respectively. For the ν₄ fundamental (Gakwaya et al. 2004; Moazzen-Ahmadi & Thong 1995) diode laser spectrometry gives the origin band at 353 ± 15 cm^{−1}. Concerning the cis bending (ν₅), the Fourier transform far-IR spectroscopy applied to l-C₄ trapped in Ar matrix placed it at 172.4 cm^{−1} (Withey et al. 1991). Later on, Moazzen-Ahmadi et al. (1994) have shifted the ν₅ to lower energies (at 160.4 cm^{−1}) based on their analysis of the pattern of the l-doubling for the 5₀¹ band. Experimentally, nothing is said in the literature concerning the CC middle stretching mode ν₂. Theoretically, previous ab initio investigations (Botschwina 1997, 2006; Watts et al. 1992; Martin et al. 1996) provide more or less accurate anharmonic wavenumbers for l-C₄. The ω₁ mode harmonic fundamental has been calculated by Botschwina (1997) at 2109 cm^{−1} at the coupled cluster [RCCSD(T)/336 cGTOs] level of the ory. Watts et al. (1992) have determined the far-IR harmonic frequencies to be at 474 cm^{−1} (ω₄) and 203 cm^{−1} (ω₅) using the RCCSD(T)/cc-pVTZ. Using many-body perturbation theory (MBPT), ω₄ is computed as 390 cm^{−1} and (ω₅) 172 cm^{−1}. More recently, Botschwina (2006) has computed the low-frequency ν₅ fundamental to be at 171.1 cm^{−1} using a RCCSD(T) cis-bending one-dimensional potential. In contrast to l-C₄, no spectroscopic data are found for r-C₄ in the literature except for the theoretical work of Martin et al. (1996), who deduced the anharmonic force field of r-C₄(X¹A_g) at the RCCSD(T) level.

¹ Departamento de Astrofísica Molecular e Infrarroja (DAMIR), IEM-CSIC, C/Serrano 121, 28006 Madrid, Spain; senent@damir.iem.csic.es.

² Theoretical Chemistry Group, University of Marne-la-Vallée, Champs sur Marne, F-77454 Marne-la-Vallée, Cedex 2, France.

Recently, we were presenting electronic structure calculations giving an insight into the stable isomers of the C_4 and their lowest electronic states (Massó et al. 2006). Calculations were achieved using monoconfigurational [CCSD(T)] and multiconfigurational (MRCI/CASSCF) methods. We localized four stationary points (three minima and one saddle point) in the surface, two of them corresponding to two isomers of similar stabilities: one linear [$l-C_4(X^3\Sigma_g^-)$] and one cyclic [$r-C_4(X^1A_g)$]. A third structure of C_{2v} symmetry, $d-C_4(X^1A_1)$, was found, although it is not obvious if it is an isomer or a transition state. As stated there, it is the best candidate for being the third isomer of C_4 observed experimentally (Kella et al. 1993). The fourth stationary point corresponds to an unstable square structure lying between the two conformers of the rhombic isomer. A preliminary exploration of the potential energy surfaces in order to establish possible isomerization processes showed that these isomers are separated by large potential barriers, high enough to allow for the treatment of each form separately for its spectroscopy. Accordingly, the six-dimensional potential energy surfaces (6D-PESs) are mapped here, in symmetry-adapted coordinates, for the two most stable isomers of C_4 , close to their equilibrium geometries. These 6D-PESs are derived as full quartic force fields allowing the deduction of a set of spectroscopic data for these two isomers using standard perturbation theory. In what follows we focus mainly on the bendings in order to discuss the tentative assignment of the $57\ \mu\text{m}$ astrophysical band to C_4 and therefore its presence in Sgr B2, IRC +10216, CRL 2688, CRL 618, and NGC 7027. It is worth noting that most of previous calculations on carbon chains have been performed within the harmonic approximation. However, a very anharmonic bending pattern is established experimentally for C_3 (Cernicharo et al. 2000). Moreover, strong couplings are expected between the modes leading to pronounce anharmonic behavior of the PES along the corresponding coordinates. For both reasons, the harmonic approximation is useless for the PES topology that is expected for small C_n clusters, a fortiori for C_4 .

2. COMPUTATIONAL DETAILS

Both static and dynamical electronic correlations play a crucial role for C_4 (Massó et al. 2006). Hence, our electronic computations were done using the complete active space self-consistent field (CASSCF; Werner & Knowles 1985; Knowles & Werner 1985) followed by the internally contracted multireference configuration interaction (MRCI) approaches (Werner & Knowles 1988; Knowles & Werner (1988)). For CASSCF, various different active spaces selected using orbital energy and symmetry criteria have been explored. For data presented here, we were using the largest space possible where the active spaces was defined containing ten orbitals; eight orbitals (four core orbitals and four valence orbitals) have been considered doubly occupied in all the configurations, but they have been optimized. In MRCI calculations, all configurations having a weight greater than 0.03 in the CI expansion of the CASSCF wave functions were taken as a reference resulting in more than 7×10^6 uncontracted CSFs to be treated in each symmetry of the C_{2v} point group. All valence electrons were correlated. For MRCI, the Davidson correction (MRCI + Q) was also included. The electronic calculations have been performed using the MOLPRO program Werner & Knowles (2002). For carbon, the *spdfcc*-pVTZ basis set of Dunning (1989) was used. The 6D-PESs of $l-C_4(X^3\Sigma_g^-)$ and $r-C_4(X^1A_g)$ were mapped close to their equilibrium geometries given in Massó et al. (2006). These 6D-PESs are derived as quartic force fields in symmetry adapted coordinates (see § 3 for more details). The main group of spectroscopic parameters (fundamentals, overtones, several combination band positions, etc.) has been calcu-

lated with perturbation theory applied on the quadratic, cubic, and quartic force fields derived from the 6D-PESs and the new FORTRAN code FIT-ESPEC.³ This new code performs a linear fit of the energies on internal coordinates to a Taylor series followed by a minimization for determining the most stable geometry. The final force field is defined in dimensionless normal coordinates. For accurate computations of anharmonicities, the calculated potential contains four mode-coupling terms. For comparison, harmonic frequencies were also determined using the coupled cluster methods including the perturbative treatment of the connected triple substitutions RCCSD(T) (Knowles et al. 1993), and all valence electrons were correlated at the optimized geometry structures defined in Massó et al. (2006) and the standard options implemented in the MOLPRO package.

3. RESULTS AND DISCUSSION

The local PESs for the ground electronic states of the two isomers [$l-C_4(X^3\Sigma_g^-)$ and $r-C_4(X^1A_g)$] are calculated for determining their spectroscopic parameters considering the anharmonic effects. As pointed out in § 1, deep potential wells are separating each isomer, allowing the treatment of them separately for their spectroscopy. The surfaces are therefore mapped around their respective equilibrium geometries, i.e., external CC distances = $1.2960\ \text{\AA}$ and middle CC = $1.3167\ \text{\AA}$ in a linear configuration [i.e., for $l-C_4(X^3\Sigma_g^-)$], and R_{31} (the shorter intracyclic CC bond) = $1.5201\ \text{\AA}$, R_{12} = $1.4414\ \text{\AA}$ for a planar D_{2h} structure [i.e., $r-C_4(X^1A_g)$]; Massó et al. 2006].

These calculations were done using the CASSCF approach followed by the MRCI + Q and the cc-pVTZ basis set. Several reasons justify the employment of MRCI + Q for the complete spectroscopic study of the C_4 radical, although it is accompanied by the loss of size consistency, which is an important property in the determination of PESs. First, harmonic preliminary studies of $l-C_4$ show that the monoconfigurational methods, such as RCCSD(T), are unsuccessful in predicting some frequencies and, therefore, of their anharmonic couplings to the low-frequency bending modes of interest here. This is the case at least for the ν_3 fundamental of the linear form (antisymmetric CC stretching mode). Such methods are leading to an overestimation of the corresponding wavenumbers. Indeed, the RCCSD(T)/cc-pVTZ harmonic wavenumbers are computed $\omega_1 = 2109$, $\omega_2 = 937$, $\omega_3 = 1938$, $\omega_4 = 381$, and $\omega_5 = 176\ \text{cm}^{-1}$. The ν_3 is off by about $400\ \text{cm}^{-1}$ from the experimental determinations ($1548\text{--}1539\ \text{cm}^{-1}$; Heath & Saykally 1991; Smith et al. 1994; Forney et al. 1995; Tam et al. 1997; Szczepanski et al. 1996). A large and significant improvement of this frequency is obtained with the UCCSD(T) and CASSCF methods (1554.6 and $1669.9\ \text{cm}^{-1}$, respectively). This is because of (1) symmetry breaking problems not fully solved at the CC level of theory and (2) underestimation of static correlation. Second, the electronic ground wave functions of the C_4 isomers show a strong multiconfigurational character where the statistical weight of the HF configuration on the CASSCF wave function is relatively low, and it varies strongly by changing, for example, the distances from equilibrium. Only MRCI allows for the correction of all these discrepancies, and it is believed to give the most reliable data.

3.1. Anharmonic Force Fields for C_4

For $l-C_4(X^3\Sigma_g^-)$, 1050 MRCI + Q nonredundant energies were computed. For the generation of the grid of points, symmetry and

³ FIT-ESPEC is a FORTRAN code for calculating spectroscopic parameters from a force field in internal coordinates (M. L. Senent 2007).

FIG. 1.—Independent internal coordinates of l-C₄.

energy criteria have been taken into consideration to select a set of geometries depending on six internal coordinates: three bond distances, R_1 (external CC), R_2 (middle CC), and R_3 (external CC); two in-plane angles, Θ_1 and Θ_2 , which are defined in Figure 1; and a dihedral angle, $\tau = \text{C4 C1 C3 C2}$. The seven independent symmetry vibrational coordinates corresponding to a linear molecule are generated using the definition of Hoy et al. (1972) for the linear angles. Bond distances and linear angles lying in the X - Z and Y - Z planes are used to define the simplest adapted symmetry coordinates

$$\begin{aligned} S_1 &= R_2, & S_2 &= \frac{1}{\sqrt{2}}(R_1 + R_3), & S_3 &= \frac{1}{\sqrt{2}}(R_1 - R_3), \\ S_i^{zs} &= \frac{1}{\sqrt{2}}(\theta_1^{zs} + \theta_2^{zs}), & (i, s) &= (4, x), (4, y), \\ S_i^{zs} &= \frac{1}{\sqrt{2}}(\theta_1^{zs} - \theta_2^{zs}), & (i, s) &= (5, x), (5, y). \end{aligned} \quad (1)$$

Our grid allows the definition of the PES up to about 12,000 cm^{-1} ; R_1 , R_2 , and R_3 vary in the ranges 1.24–1.36, 1.26–1.36, and 1.24–1.36 Å, respectively, and the angular coordinates change from 0° to 85°.

For r-C₄(X^1A_g), the six internal coordinates (five bond distances [R_{12} , R_{14} , R_{23} , R_{34} , and the diagonal R_{13}] and a torsional coordinate τ [the dihedral angle between planes C2 C1 C3 and C1 C3 C4; cf. Fig. 2]) were selected to define the grid. Our grid covers the nuclear geometries where $1.40 \text{ Å} \leq R_{12} \leq 1.72 \text{ Å}$, $1.47 \text{ Å} \leq R_{13} \leq 1.59 \text{ Å}$, and $0^\circ \leq \tau \leq 20^\circ$. MRCI + Q energies were computed defining the PES up to about 10,000 cm^{-1} . Our internal coordinates allow for the definition of the six symmetry coordinates as (Linguerrri et al. 2005)

$$\begin{aligned} S_1 &= \frac{1}{\sqrt{4}}(R_{12} + R_{14} + R_{23} + R_{34}), & S_2 &= R_{13}, \\ S_3 &= \frac{1}{\sqrt{4}}(R_{12} + R_{14} - R_{23} - R_{34}), & S_4 &= \tau, \\ S_5 &= \frac{1}{\sqrt{4}}(R_{12} - R_{14} - R_{23} + R_{34}), \\ S_6 &= \frac{1}{\sqrt{4}}(R_{12} - R_{14} + R_{23} - R_{34}). \end{aligned} \quad (2)$$

For both isomers, the MRCI + Q energies were fitted to a full dimensional Taylor series, for which the coefficients are the forces

$$\begin{aligned} V(q_1, q_2, \dots, q_n) &= \sum_{i=1}^n \sum_{j=1}^n \frac{1}{2} f_{ij} q_i q_j + \sum_{i=1}^n \sum_{j=1}^n \sum_{k=1}^n \frac{1}{6} f_{ijk} q_i q_j q_k \\ &+ \sum_{i=1}^n \sum_{j=1}^n \sum_{k=1}^n \sum_{l=1}^n \frac{1}{24} f_{ijkl} q_i q_j q_k q_l, \end{aligned} \quad (3)$$

FIG. 2.—Independent internal coordinates of r-C₄.

where $q_i = S_i - S_i^{\text{REF}}$. S_i^{REF} refers to the reference geometry used for fitting which are chosen to be the S_i equilibrium values. This results in 76 and 48 force field coefficients to be optimized for l-C₄($X^3\Sigma_g^-$) and for r-C₄(X^1A_g), respectively. The rms deviations of the fits were 43 cm^{-1} and $R^2 = 1.00000$. The corresponding quartic anharmonic force fields are listed in Table 1. Structural parameters of the reference geometry are those calculated and shown in Table 1 of Massó et al. (2006). The minimum for the linear isomer corresponds to a linear structure with $R_1 = R_3 = 1.3167 \text{ Å}$ and $R_2 = 1.2960 \text{ Å}$, whereas the parameters for the rhombic isomer minimum are $R_{12} = 1.4510 \text{ Å}$ and $R_{13} = 1.5204 \text{ Å}$. Our distances should be accurate to within 0.01 Å.

3.2. Spectroscopic Constants and Anharmonic Fundamentals

3.2.1. l-C₄($X^3\Sigma_g^-$)

Table 2 lists anharmonicity terms for linear C₄ deduced from our quartic force field. This table shows that some of the x_{ij} are quite large, especially those corresponding to the asymmetric stretching and those between the bending and the stretching (e.g., x_{14} is equal to -40.065 cm^{-1}). This is the signature of the strong coupling between these modes, invalidating the use of the harmonic approximation. Table 3 gives the structural parameters and the spectroscopic data for l-C₄($X^3\Sigma_g^-$). The data deduced from calculations achieved for various isotopomers containing ^{13}C , the second most abundant carbon isotope existing in the interstellar medium (ISM; abundance ratio $^{13}\text{C}/^{12}\text{C} \sim 1/45$), are also presented. This table shows the rotational constants at equilibrium (B_e) and the rotational constants that include the vibrational corrections for the zero-point vibrational energy (B_0) and for the five fundamentals ($B\nu_i$). For $^{12}\text{C}_4$, our B_0 value differs by less than 0.0025 cm^{-1} from the B_0 constant deduced from the diode laser absorption study of Moazzen-Ahmadi et al. (1994). The differences between our $B\nu_i$ values for the ν_3 , ν_4 , and ν_5 fundamentals and those deduced with the gas-phase measurements of Moazzen-Ahmadi et al. (1994) and Moazzen-Ahmadi & Thong (1995) are about 1%, which is reflecting the 0.01 Å accuracy on our computed equilibrium distances. This good accord validates our 6D-PES and the use of perturbation theory for the deduction of accurate data for l-C₄. The rotational constants for the most abundant isotopomers of l-C₄ listed in Table 3 are predictive in nature and should be of similar accuracy.

Table 3 lists the harmonic and anharmonic wavenumbers of l-C₄ deduced from our MRCI + Q 6D-PES and perturbation theory. The stretchings are computed $\omega_1 = 2157.2$, $\omega_2 = 911.1$, and $\omega_3 = 1529.1 \text{ cm}^{-1}$. The corresponding anharmonic wavenumbers are $\nu_1 = 2040.6$, $\nu_2 = 883.1$, and $\nu_3 = 1496.9 \text{ cm}^{-1}$. The symmetric

TABLE 1
ANHARMONIC FORCE FIELDS OF THE GROUND ELECTRONIC STATES OF l-C₄ AND r-C₄ COMPUTED FROM THE MRCI/CASSCF/cc-pVTZ PESs

l-C ₄				r-C ₄			
f_{ij}				f_{ij}			
f_{11}	10.301	f_{55}	0.174	f_{11}	6.158	f_{55}	4.117
f_{22}	9.376	f_{21}	0.207	f_{22}	5.179	f_{66}	5.119
f_{33}	8.265			f_{33}	1.761	f_{21}	-1.753
f_{44}	0.123			f_{44}	0.218		
f_{ijk}				f_{ijk}			
f_{111}	-103.168	f_{442}	-0.592	f_{111}	-19.065	f_{442}	1.930
f_{222}	-80.538	f_{551}	-0.970	f_{222}	-7.905	f_{551}	-24.210
f_{112}	-1.956	f_{552}	-0.419	f_{112}	9.784	f_{552}	-14.837
f_{221}	-1.097	f_{345}	-0.806	f_{221}	-8.970	f_{661}	-20.869
f_{331}	-15.910			f_{331}	1.631	f_{662}	9.415
f_{332}	-30.179			f_{332}	13.371	f_{653}	-7.518
f_{441}	-0.483			f_{441}	-0.440		
f_{ijkl}				f_{ijkl}			
f_{1111}	1041.016	f_{5533}	-13.877	f_{1111}	72.352	f_{5533}	-14.625
f_{2222}	1377.446	f_{4455}	0.003	f_{2222}	-173.259	f_{6611}	33.209
f_{3333}	609.449	$f_{555'5'}$	-2.818	f_{3333}	17.650	f_{6633}	23.638
f_{4444}	0.511	f_{1112}	40.056	f_{4444}	0.039	f_{6644}	-0.286
f_{5555}	0.448	f_{2221}	152.576	f_{5555}	3.479	f_{6655}	15.939
f_{2211}	164.895	f_{3321}	112.047	f_{6666}	-47.082	f_{1112}	-97.567
f_{3311}	522.105	f_{4421}	0.326	f_{2211}	38.766	f_{2221}	47.667
f_{3322}	-968.828	f_{5521}	-15.319	f_{3311}	-35.021	f_{3321}	5.904
f_{4411}	2.297	$f_{4455'}$	1.713	f_{3322}	38.172	f_{6622}	92.249
f_{4422}	-14.825	f_{1345}	-208.344	f_{4411}	0.263	f_{4421}	-2.274
f_{4433}	13.742	f_{2345}	75.271	f_{4422}	6.681	f_{5521}	21.959
$f_{444'4'}$	0.677			f_{4433}	-0.059	f_{6621}	-40.586
f_{5511}	-4.265			f_{5511}	31.008	f_{6531}	-2.274
f_{5522}	-3.461			f_{5522}	-15.998	f_{6532}	21.959

NOTE.—These terms are of the form f_{ij} , where i and j correspond to the S coordinates defined in eqs. (1) and (2). All values are in units of aJ.

CC stretch ν_1 is located at 2032 ± 50 and 2057 ± 50 cm⁻¹ using photoelectron spectroscopy (Arnold et al. 1991; Xu et al. 1997), which agrees quite well with our value, and it is coherent with the previous calculations of Botschwina (1997; 2109 cm⁻¹) and Watts et al. (1992; 2156 cm⁻¹). For the central CC stretching ν_2 , our value agrees well with those computed previously, and it should be more reliable since it is derived from a full quartic force field. However, it is quite certain that our ν_3 wavenumber of 1469.9 cm⁻¹ is quite low (the difference with gas-phase measurements reach 53 cm⁻¹; see Table 3), since the symmetry breaking problem emphasized above is not fully resolved, even at the MRCI level. We do believe that larger computations in which all CASSCF CSFs are used to generate the MRCI active space and basis set larger than cc-pVTZ are needed for better describing the PES along this nuclear motion. Let us now consider the bending modes, which are extremely important in order to interpret astrophysical observations with the far-IR telescope. Our anharmonic MRCI value for the trans-bending (ν_4) is 314.4 cm⁻¹, which falls in the ranges of the experimental determinations, i.e., 339 ± 55 cm⁻¹ (Arnold et al. 1991), 323 ± 50 cm⁻¹ (Xu et al. 1997), and 352 ± 15 cm⁻¹ (Gakwaya et al. 2004; Moazzen-Ahmadi & Thong 1995). This value should be accurate to within 10 cm⁻¹, thus reducing the error bars for this fundamental. The cis bending (ν_5), which is measured at 160 ± 4 cm⁻¹ in the gas phase by Moazzen-Ahmadi et al. (1994) by means of diode laser spectroscopy, is computed to be 162.2 cm⁻¹ at the cc-pVTZ/MRCI level of theory. In a recent paper, Botschwina (2006) provides a value of 171 cm⁻¹ for this bending

mode using a cis-bending CCSD(T) one-dimensional potential, which neglects interactions with the stretching modes.

Finally, Table 3 gives the vibrational data for the most abundant isotopomers of l-¹²C₄ and the wavenumbers of some overtones and combination modes. Isotopic substitutions produce larger effects on the stretching modes, whereas the isotopic shifts of the bending modes are less significant. For the symmetric ν_1 stretching, a single carbon substitution displaces the band by an amount of 32 cm⁻¹ (from 2040.6 to 2008.4 cm⁻¹). For ν_2 , this variation is less significant (from 883.1 to 868.5 cm⁻¹). In the case of ν_3 , the calculated displacement from ¹²C₄ to ¹³C¹²C¹²C¹²C of 16 cm⁻¹ coincides with the observed displacement of 15 cm⁻¹ (Shen & Graham 1989), since mass effects are less related to static correlation. The data in Table 3 for the other isotopomers and

TABLE 2
ANHARMONIC CONSTANTS x_{ij} AND g_{ij} OF l-C₄ COMPUTED FROM THE MRCI/CASSCF/cc-pVTZ FORCE FIELD

Anharmonic Constants (cm ⁻¹)							
x_{11}	-8.858						
x_{22}	3.403	x_{12}	-12.505				
x_{33}	16.594	x_{13}	-109.590	x_{23}	-41.252		
x_{44}	-1.873	x_{14}	-40.065	x_{24}	-0.857	x_{34}	26.339
x_{55}	-0.612	x_{15}	2.245	x_{25}	-7.038	x_{35}	-16.282
g_{44}	2.457	g_{55}	0.662	g_{45}	0.358	x_{45}	5.641

TABLE 3
STRUCTURAL AND PERTURBATION THEORY SPECTROSCOPIC PARAMETERS OF THE GROUND ELECTRONIC STATE OF THE ISOTOPOMERS
OF I-C₄ COMPUTED FROM THE MRCI/CASSCF/cc-pVTZ PES

I-C ₄ PARAMETERS	EXPERIMENTAL AND PREVIOUS CALCULATIONS CCCC	MRCI				
		CCCC	¹³ CCCC	C ¹³ CCC	C ¹³ C ¹³ CC	¹³ CCC ¹³ C
Structural Parameters (Å)						
<i>R</i> _{int}		1.2960				
<i>R</i> _{ext}		1.3167				
Rotational Constants (cm ⁻¹)						
<i>B</i> _{<i>e</i>}		0.16411	0.1583	0.1635	0.1628	0.1526
<i>B</i> ₀	0.166111 ^a	0.16360	0.1578	0.1629	0.1623	0.1522
<i>D</i> _{<i>e</i>} (×10 ⁻⁷)	0.282 ^a	0.213	0.198	0.211	0.210	0.184
<i>B</i> (<i>ν</i> ₁ = 1)		0.1616	0.1559	0.1610	0.1604	0.1503
<i>B</i> (<i>ν</i> ₂ = 1)		0.1629	0.1571	0.1622	0.1616	0.1515
<i>B</i> (<i>ν</i> ₃ = 1)	0.165406 ^a	0.1628	0.1570	0.1622	0.1615	0.1515
<i>B</i> (<i>ν</i> ₄ = 1)	0.166808 ^b	0.1642	0.1584	0.1635	0.1628	0.1527
<i>B</i> (<i>ν</i> ₅ = 1)	0.166862 ^a	0.1642	0.1584	0.1636	0.1629	0.1528
<i>q</i> ₄ (×10 ⁻³)	0.184 ^a	0.185	0.172	0.188	0.188	0.160
<i>q</i> ₅ (×10 ⁻³)	0.366 ^a	0.336	0.315	0.337	0.337	0.296
Perturbation Theory Spectroscopic Parameters (cm ⁻¹)						
<i>ω</i> ₁ (<i>σ_g</i>)	2106 ^c 2156 ^d 2109 ^e	2157.2	2151.9	2121.5	2083.9	2146.6
<i>ω</i> ₂ (<i>σ_g</i>)	935 ^c 936 ^d 926 ^e	911.1	895.2	908.7	906.1	879.7
<i>ω</i> ₃ (<i>σ_u</i>)	1556 ^c 1600 ^d	1529.1	1514.4	1513.3	1499.4	1499.4
<i>ω</i> ₄ (<i>π_g</i>)	390 ^c 474 ^d	319.2	318.6	313.7	308.0	318.0
<i>ω</i> ₅ (<i>π_u</i>)	172 ^c 203 ^d	168.3	166.6	166.6	165.0	165.0
<i>ν</i> ₁ (<i>σ_g</i>)	2032(50) ^f 2057(50) ^g	2040.6	2037.1	2008.4	1972.7	2033.4
<i>ν</i> ₂ (<i>σ_g</i>)		883.1	868.5	880.7	878.3	854.2
<i>ν</i> ₃ (<i>σ_u</i>)	1548.9368 ^h 1547.0 ⁱ 1543.4 ^j 1539.5 ^k	1496.9	1483.3	1480.7	1467.3	1469.6
<i>ν</i> ₄ (<i>π_g</i>)	339(55) ^f 323(50) ^g 352(15) ^{b, l}	314.4	313.9	309.2	303.3	313.4
<i>ν</i> ₅ (<i>π_u</i>)	160(4) ^a 172.4 ^m 170.4 ^m 174 ⁿ 171.1 ^o	162.2	160.8	160.4	159.0	159.4
2 <i>ν</i> ₁		4063.4	4055.9	3999.7	3930.0	4048.2
2 <i>ν</i> ₂		1773.1	1743.6	1768.0	1763.0	1715.1
2 <i>ν</i> ₃		3027.0	2999.2	2993.3	2966.5	2971.1
2 <i>ν</i> ₄		620.2	618.6	610.5	599.6	616.9

TABLE 3—*Continued*

l-C ₄ PARAMETERS	EXPERIMENTAL AND PREVIOUS Calculations CCCC	MRCI				
		CCCC	¹³ CCCC	C ¹³ CCC	C ¹³ C ¹³ CC	¹³ CCC ¹³ C
	Perturbation Theory Spectroscopic Parameters (cm ⁻¹)					
2ν ₅		321.9	319.0	318.4	315.7	316.1
ν ₁ + ν ₂		2911.2	2893.3	2876.7	2839.3	2875.5
ν ₁ + ν ₃		3427.1	3414.3	3381.3	3331.5	3400.5
ν ₂ + ν ₃		2338.8	2310.8	2321.9	2307.4	2283.0
ν ₃ + ν ₅		1642.8	1628.2	1625.7	1610.7	1613.3

^a Diode laser absorption (gas phase) from Moazzen-Ahmadi et al. (1994).^b Diode laser absorption (gas phase) from Moazzen-Ahmadi & Thong (1995).^c Previously calculated value from MBPT(2)/6-311G(2d) from Watts et al. (1992).^d Previously calculated value from CCSD(T)/PVTZ from Watts et al. (1992).^e Previously calculated value from RCCSD(T)/336-cGTO from Botschwina (1997).^f Photoelectron spectroscopy (gas phase) from Arnold et al. (1991).^g Photoelectron spectroscopy (gas phase) from Xu et al. (1997).^h Diode laser absorption (gas phase) from Heath & Saykally (1991).ⁱ IR (Ne matrix, solid Ne) from Smith et al. (1994), Forney et al. (1995), and Tam et al. (1997).^j IR (Ar matrix) from Shen & Graham (1989).^k IR (Kr matrix) from Szczepanski et al. (1996).^l Diode laser absorption (gas phase) from Gakwaya et al. (2004).^m IR (Ar matrix) from Withey et al. (1991).ⁿ Far-IR astrophysical observations from Cernicharo et al. (2002).^o RCCSD/VQZ from Botschwina (2006).

those of the unknown overtones and combination modes should be helpful in their identification in the laboratory and ISM.

3.2.2. r-C₄(X¹A_g)

To our knowledge, experimental spectroscopic works on r-C₄ are nonexistent. Theoretically and except for the work of Martin et al. (1996) performed with the monoconfigurational RCCSD(T) method, no data are available in the literature dealing with this isomer, which is believed to be as stable as the linear form (Massó et al. 2006). For this reason, data in Table 4 represent predictions for this species and its isotopomers. Indeed, Table 4 lists the harmonic and anharmonic frequencies and several spectroscopic parameters of the rhombic isomer of C₄, determined from the force field discussed in § 3.1. Calculations have been performed using perturbation theory in dimensionless normal coordinates derived from the 6D-PES.

When we consider the rotational constants, they are computed to be $A_e = 1.2149$, $B_e = 0.4599$, and $C_e = 0.3336$ cm⁻¹ for the most abundant isotopomer of r-C₄. When the vibration-rotation terms are taken into account, the corresponding A_v , B_v , and C_v constants are changing by 0.01–0.02 cm⁻¹. Readers are referred to Table 4 for more details.

The two lowest fundamental frequencies, which are IR active (intensities 42 and 90 kcal mol⁻¹), are calculated to be 279.2 cm⁻¹ (ν₄[b_{1u}]; out-of-plane) and 522.5 cm⁻¹ (ν₅[b_{2u}], in-plane bending). The symmetric stretchings are computed to be 1285.9 and 949.4 cm⁻¹, whereas the nonsymmetric ones have been calculated to lie at 981.5 (ν₃) and 1378.0 cm⁻¹ (ν₆). Finally, this table shows that the effect of the carbon substitution is not really significant for the bending modes (isotopic shifts less than 5 cm⁻¹), since the rhombic form is more rigid and its flexibility is surely lower compared to the linear form. However, differences between r-¹²C₄ and r-¹³C¹²C₃ reach 10 cm⁻¹ for the stretchings.

3.2.3. Comparison with Astrophysical Observations

We turn now to the comparison of our data with the band observed with *ISO* at 174 cm⁻¹, which has been attributed to the

ν₅ bending mode of l-C₄ (Cernicharo et al. 2002). Table 3 shows that the previous measurements for this band range from 160 cm⁻¹ (Moazzen-Ahmadi et al. 1994) in the gas phase up to 172.4 and 170 cm⁻¹ in cooled Ar matrixes (Withey et al. 1991). Our large calculations are giving a value of 162.2 cm⁻¹, consistent with the gas-phase value. Nevertheless, even here, a final statement about this band is hardly possible since our calculations are expected to be accurate to within 10 cm⁻¹ for such low-frequency modes. This band cannot be attributed to the isoenergetic stable isomer r-C₄, since the low harmonic bending frequencies are computed to be well above 200 cm⁻¹, far from the detected 174 cm⁻¹ band. Nevertheless, even the assignment of this band to l-C₄ (ν₅) is questionable when one considers the shape of the *ISO* observed pattern at 174 cm⁻¹. In Cernicharo et al. (2002), it has been proposed that the complexity may be understood assuming a molecular system with a nonzero spin-orbit coupling of $A_{SO} = 4$ cm⁻¹ (or better put, a spin-spin constant of 4 cm⁻¹). Since the ground state of C₄ is of the ³Σ_g⁻ species, a spin-orbit constant so high should be related to the proximity of the lowest electronic states. For this reason, we have performed ab initio calculations including second-order spin-orbit and spin-spin effects (Lefebvre-Brion et al. 2004). The first excited state of l-C₄ is the $A^1\Delta_g$ state located at 0.33 eV above the *X*-state (Massó et al. 2006). However, the $\langle A^1\Delta_g | H^{SO} | X^3\Sigma_g^- \rangle$ integral gives no contribution for $\Delta\Lambda = \pm 2$. The following excited state is the $B^1\Sigma_g^+$ state, which results from the π² electron configuration as the *X*- and *A*-states. At the cc-pVTZ/CASSCF level of theory and using the formula developed in Lefebvre-Brion & Field (2004, p. 201) the spin-spin splitting for the *X*-state is computed to be in the range 0.17–0.2 cm⁻¹. The effect is too small for C₄ to justify the assignment of the observed band using ab initio calculations. Other molecular candidates for the 57 μm should be tested (M. L. Senent et al. 2008, in preparation).

4. CONCLUSIONS

In the present work, valuable spectroscopic data on the lowest isomers of C₄ are computed using accurate ab initio methods and

TABLE 4
STRUCTURAL AND PERTURBATION THEORY SPECTROSCOPIC PARAMETERS OF THE GROUND ELECTRONIC STATE
OF THE ISOTOPOMERS OF r-C₄ COMPUTED FROM THE MRCI/CASSCF/cc-pVTZ PES

r-C ₄ PARAMETERS	CCCC (MARTIN ET AL. 1996) ^a	THIS WORK ^b				
		CCCC	¹³ C ₁ CCC	C ¹³ C ₂ CC	¹³ C ₁ ¹³ C ₂ CC	¹³ C ₁ C ¹³ C ₃ C
Structural Parameters (Å)						
R ₁₂	1.4540	1.4510				
R ₁₃	1.5186	1.5204				
Rotational Constants (cm ⁻¹)						
A _e		1.2149	1.1673	1.2149	1.1673	1.1212
B _e		0.4599	0.4599	0.4419	0.4419	0.4600
C _e		0.3336	0.3299	0.3240	0.3205	0.3262
κ		-0.7134	-0.6895	-0.7354	-0.7134	-0.6636
D _J (×10 ⁻⁶)		0.2129	0.2115	0.1979	0.1966	0.2102
D _{JK} (×10 ⁻⁶)		0.6571	0.6466	0.6173	0.6092	0.6312
D _K (×10 ⁻⁵)		0.4553	0.4167	0.4608	0.4220	0.3780
d _J (×10 ⁻⁶)		0.592	0.599	0.540	0.547	0.606
d _K (×10 ⁻⁵)		0.7157	0.6890	0.6858	0.6611	0.6627
A ₀		1.2178	1.1702	1.2177	1.1700	1.1243
B ₀		0.4570	0.4570	0.4391	0.4391	0.4570
C ₀		0.3319	0.3282	0.3223	0.3189	0.3245
A(ν ₁ = 1)		1.2142	1.1668	1.2140	1.1666	1.1214
B(ν ₁ = 1)		0.4566	0.4565	0.4387	0.4387	0.4565
C(ν ₁ = 1)		0.3315	0.3278	0.3221	0.3186	0.3241
A(ν ₂ = 1)		1.2184	1.1705	1.2184	1.1705	1.1245
B(ν ₂ = 1)		0.4567	0.4567	0.4387	0.4387	0.4567
C(ν ₂ = 1)		0.3267	0.3226	0.3179	0.3140	0.3185
A(ν ₃ = 1)		1.2028	1.1559	1.2027	1.1558	1.1108
B(ν ₃ = 1)		0.4543	0.4544	0.4365	0.4366	0.4545
C(ν ₃ = 1)		0.3329	0.3298	0.3227	0.3198	0.3266
A(ν ₄ = 1)		1.1982	1.1520	1.1978	1.1516	1.1076
B(ν ₄ = 1)		0.4571	0.4571	0.4392	0.4392	0.4571
C(ν ₄ = 1)		0.3334	0.3298	0.3238	0.3204	0.3261
A(ν ₅ = 1)		1.2602	1.2099	1.2601	1.2099	1.1617
B(ν ₅ = 1)		0.4572	0.4572	0.4393	0.4392	0.4572
C(ν ₅ = 1)		0.3325	0.3289	0.3229	0.3195	0.3252
A(ν ₆ = 1)		1.2191	1.1714	1.2190	1.1712	1.1254
B(ν ₆ = 1)		0.4541	0.4541	0.4363	0.4363	0.4542
C(ν ₆ = 1)		0.3305	0.3269	0.3210	0.3176	0.3233
Perturbation Theory Spectroscopic Parameters (cm ⁻¹)						
ω ₁ (a _g)	1256.9	1306.6	1291.6	1296.1	1280.2	1277.0
ω ₂ (a _g)	938.8	989.5	981.6	976.9	969.9	927.7
ω ₃ (b _{1g})	1024.3	1079.1	1063.1	1073.4	1057.5	1048.6
ω ₄ (b _{1u})	303.2	284.3	281.6	281.5	278.8	278.8
ω ₅ (b _{2u})	527.7	523.1	517.8	518.0	512.6	513.0
ω ₆ (b _{3u})	1380.6	1449.2	1435.8	1436.5	1422.9	1421.1
ν ₁ (a _g)	1248.6	1285.9	1269.6	1277.2	1260.2	1253.9
ν ₂ (a _g)	926.9	949.4	939.3	941.4	931.9	928.1
ν ₃ (b _{1g})	998.7	981.5	968.6	976.8	963.8	956.5
ν ₄ (b _{1u})	302.3	279.2	276.1	276.5	273.5	273.5
ν ₅ (b _{2u})	520.2	522.5	516.9	517.7	512.0	511.7
ν ₆ (b _{3u})	1313.5	1378.0	1365.1	1367.1	1354.1	1351.5
2ν ₁		2558.7	2526.4	2541.5	2507.8	2495.4
2ν ₂		1889.5	1867.3	1874.1	1853.9	1843.8
2ν ₃		1912.4	1888.5	1903.3	1879.2	1865.8
2ν ₄		547.3	541.3	542.4	536.4	536.6
2ν ₅		1023.2	1017.6	1009.2	1003.1	1012.4
2ν ₆		2722.2	2696.9	2701.0	2675.5	2670.5
ν ₁ + ν ₆		2659.8	2629.1	2641.7	2610.3	2598.4
ν ₁ + ν ₃		2197.9	2171.0	2185.2	2157.5	2145.4
ν ₄ + ν ₅		792.8	784.3	785.7	777.1	776.6

^a Variational CCSD(T)/cc-pVTZ calculations.

^b PT MRCI/CASSCF/cc-pVTZ.

a large basis set. We provide parameters for various isotopomers containing ^{12}C and ^{13}C . Anharmonic spectroscopic parameters of the most abundant isotopic varieties are determined with perturbation theory. For this purpose, the quadratic, cubic, and quartic force fields are computed from the six-dimensional potential energy surfaces mapped around the respective local minima. This theoretical work reveals that the frequency calculations allow us to assign the astrophysical observed band to tetracarbon, whereas the argument based on the spin-orbit coupling appears to contradict previous assumptions. Further experimental investigations are needed for the interpretation of the astrophysical observations in connection with similar theoretical investigations on other molecular candidates. The far-infrared spectroscopy should be

helpful for these species, which possess zero dipole moment and low bending modes.

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