Anharmonic rovibrational calculations of singlet cyclic C_4 using a new ab initio potential and a quartic force field

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ABSTRACT

We report a CCSD(T)/cc-pCV5Z quartic force field (QFF) and a semi-global CCSD(T)-F12b/aug-cc-pVTZ potential energy surface (PES) for singlet, cyclic C_4. Vibrational fundamentals, combinations and overtones are obtained using vibrational second-order perturbation theory (VPT2) and the vibrational configuration-interaction (VCI) approach. Agreement is within 10 cm^{-1} between the VCI calculated fundamentals on the QFF and PES using the MULTIMODE (MM) program, and VPT2 and VCI results agree for the fundamentals. The agreement between VPT2-QFF and MM-QFF results is also good for the C_4 combinations and overtones. The $J = 1$ and $J = 2$ rovibrational energies are reported from both VCI (MM) on the PES and VPT2 on the QFF calculations. The spectroscopic constants of $^{12}C_4$ and two C_{2v}-symmetry, single ^{13}C-substituted isotopologues are presented, which may help identification of cyclic C_4 in future experimental analyses or astronomical observations.

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I. INTRODUCTION

Carbon clusters have attracted great interest over the years for many reasons. Small carbon clusters C_n are important intermediates in chemical reactions and have been observed in interstellar space, and tetracarbon is one of the most important species. Larger clusters, notably C_{60}, have unusual and technologically important electrical and physical properties. They are challenging theoretically, owing to substantial multi-reference character and low-lying electronic states. There is a large amount of literature on the electronic spectroscopy of small clusters but less on the vibrational spectroscopy. This is important for possible detection of the clusters in the interstellar medium. Previous work dealing with small carbon clusters is summarized in the reviews of Weltner and Vanzee[1] and Orden and Saykally.[2] For the C_{2n} clusters, such as C_4, C_6 and C_8, *ab initio* calculations predict two low-energy structures, linear ($^3\sum_g^-$) and monocyclic (^1A_g). For C_4, it has been known that the linear and cyclic isomers are almost isoenergetic, with the highest level calculations of previous studies finding the cyclic isomer to be the lower energy structure.[3,4]

Experimentally, coulomb explosion imaging[5,6] and electron photodetachment[7] provided evidence of the existence of cyclic C_4 isomer. In the latter experiments, three distinct photo detachment wavelengths indicated three different structures for the C_4 anions and the neutrals. However, these experiments did not report any determination of vibrational excitations, and as far as we know, no experimental spectroscopic data of the cyclic C_4 are available in the literature.

Theoretical methods have been utilized to study the C_4 vibrations. Based on an MP2/6-311G* study, Martin *et al.*[8,9] suggested that a 1284 cm^{-1} matrix infrared (IR) feature[10] belongs to cyclic C_4. In a later study, Martin *et al.*[11] constructed a CCSD(T)/cc-pVTZ quartic force field (QFF) for cyclic C_4, and re-evaluated the assignment of the 1284 cm^{-1} feature. The estimate for the ν_6 mode of cyclic C_4, 1320 ± 10 cm^{-1}, raised doubt about the earlier assignment. More recently, Senent *et al.*[12] reported MRCI+Q/cc-pVTZ QFFs for both the linear and cyclic C_4. Their computed vibrational perturbation theory (VPT2)[13] fundamentals of cyclic C_4 showed differences as large as 50 cm^{-1} when compared to Martin's results. In addition, Martin *et al.* reported a strong Fermi resonance between ν_6 and $\nu_3 + \nu_5$

for cyclic C_4, which contributed to a significant anharmonicity for the ν_6 mode.

In this paper, we report a new *ab initio* QFF constructed at the CCSD(T)/cc-pCV5Z level, and a semi-global potential energy surface (PES) fitted from CCSD(T)-F12b/aug-cc-pVTZ (aVTZ) energies for the singlet cyclic C_4. The vibrational configuration-interaction (VCI) calculations are performed using the MULTIMODE (MM)[14–16] program, and VPT2 analyses are performed with the SPECTRO[17] program. Consistent, reliable and highly accurate vibrational (and ro-vibrational) energy levels and spectroscopic constants are generated for the singlet cyclic $^{12}C_4$ and ^{13}C isotopologues. Such QFF+VPT2/VCI and PES+VCI calculations have been widely used to determine the ro-vibrational spectroscopic constants and vibrational fundamentals of many astronomically interesting molecules in recent years.[11,18–20]

The paper is organized as follows. The next section describes the computational details of the new QFF and PES and vibrational methods. Then in Section III, both VPT2 results on the QFF and MM results on the QFF and the PES are reported and discussed. Finally, a summary and conclusion are given in Section IV.

II. COMPUTATIONAL METHODS

All the *ab initio* calculations for the electronic groud state energies are performed using the coupled-cluster single and double excitation method that includes a perturbation treatment of triple excitations, CCSD(T), with MOLPRO 2008.1.[26] The linear C_4 system shows a strong multiconfigurational character, however, the non-dynamical correlation effects are not significant for the configurations around cyclic C_4, with the $\mathscr{T}_1$ diagnostic[21] smaller than 0.02.

A. Quartic Force Field

Our initial QFF constructions followed the procedure described in Ref 22 and Ref 23. Six symmetry-adapted internal coordinates have been defined[11] and grids with step size 0.005Å/rad adopted for the evaluation of QFF constants. The CCSD(T) single point calculations are carried out on 114 symmetry-unique geometries with aug-cc-pVXZ (aVXZ)

and cc-pCVXZ (CVXZ) basis sets, X=T,Q,5. The aVXZ and CVXZ energies are extrapolated to the complete basis set (CBS) limit using a three-point formula.[24] The extrapolated aVXZ energies are further refined by adding the CCSD(T) core-correlation effects using the Martin-Taylor basis[25] or cc-pCVXZ (X=T,Q) basis, and scalar relativistic (cc-pVTZ-DK) corrections.

Next, for each set of *ab initio* calculations, 225 symmetry-redundant geometries are fitted to 52 non-zero force constants (up to quartic level) in the six symmetry-adapted internal coordinates. The average root mean square (RMS) fitting errors range from 8.2E-07 cm^{-1} to 1.7E-05 cm^{-1}. Spectroscopic constants, vibrational energy levels, and vibrationally averaged geometries are computed using VPT2 with the SPECTRO program.

The fitted force constants for the QFF can be directly used for SPECTRO calculations. However, for VCI calculations, in order to ensure correct limiting behavior of the potential, Morse-cosine coordinates are required using the QFF potential. The fitted force constants are converted to Cartesian derivatives at the exact QFF minimum by the INTDER 2005 program.[27] Then it is transformed back to a new set of force constants defined with 5 C-C bond stretches and 1 torsion coordinate. In this way, the diagonal quadratic and cubic force constants for the 4 single C-C bond stretches are determined which are necessary to derive the appropriate alpha value for the Morse function.[28] With this alpha value, a new coordinate space includes the symmetry-adapted Morse functions (for stretches), cosine (for bending angles) and sine (for torsion angles) coordinates, while the symmetry-adaption formula and the order and the symmetry type of 6 coordinates are the same as defined before.[11] The same set of 225 energies are re-fitted with these symmetry-adapted Morse/cosine/sine basis to get a new set of 52 non-zero coefficients which can then be used in the VCI calculations.

The VPT2 calculations using the QFF obtained from extrapolated, CBS-limit energies give an unstable vibrational fundamental for the out-of-plane mode ν_4. This mainly results from the carbon-carbon multiple bond sensitivity with respect to the basis set superposition error.[29] This unstable behavior essentially compromises the reliability of the CBS limit extrapolation in this case. In a previous study of benzene with similar issues,[29] use of an Atomic Natural Orbital (ANO) basis was suggested. For the singlet cyclic C_4 system,

we choose another path, which is to find a high-level QFF least impacted by such C=C multiple bond sensitivities. The CCSD(T)/cc-pCVXZ (X=T,Q,5) series of QFFs have the most consistent ν_4 anharmonicities. Thus, the CCSD(T)/cc-pCV5Z (with core) QFF is selected to report in this paper. It is denoted as "QFF" or "CV5Z QFF" hereafter. The results using all other QFFs are available upon request. Note that the scalar relativistic correction is not included in the CV5Z QFF we choose to report here, as its effects on the 6 fundamentals are all less than 1.6 cm^{-1}.

B. Semi-global PES and MULTIMODE Calculations

As already noted, we also developed a limited potential energy surface for the singlet cyclic C_4, on which we compute ro-vibrational energies variationally. The electronic structure energies are computed using the CCSD(T)-F12b[30,31] method, with aVTZ basis. For the generation of PES points, the majority of the configurations are obtained by running classical direct-dynamics calculations, using density functional theory (DFT) with the aug-cc-pVDZ basis. Additional points are generated by randomly sampling around the cyclic C_4 minimum. Finally, 2,914 CCSD(T)-F12b/aVTZ electronic energies are used for the PES fitting. The PES of C_4 is six dimensional, and is invariant with respect to all permutations of the four C atoms. We use the invariant polynomial fitting method,[32,33] in which the polynomials are functions of Morse variables with alpha value fixed at 2.0 bohr. The coefficients in the potential expression are obtained using standard weighted least-squares fitting subroutines. The total power of fitting polynomial is restricted to 7, the number of coefficients is 123, and the overall root mean square (rms) fitting error is about 30 cm^{-1}. Figure 1 shows the number of configurations in different energy ranges and the corresponding rms fitting error, both in kcal/mol. Most of the configurations are sampled around the cyclic C_4 minimum, plus 52 additional points at energies 30 - 75 kcal/mol relative to the minimum. These high energy points are necessary to ensure the PES behaves properly in the high energy region. Since the number of high energy points is small, the overall PES accuracy around the minimum is not affected. The fitting rms below 5000 cm^{-1} and 10,000 cm^{-1} are 14 cm^{-1} and 25 cm^{-1}, respectively.

Ro-vibrational calculations are performed using the MULTIMODE (MM) program, which

has been described in detail elsewhere.[14–16] Therefore, we only give a brief review here. MM is based on the Watson Hamiltonian in mass-scaled normal mode coordinates. The key feature of MM is the hierarchical n-mode representation (nMR) of the potential. For C_4, the exact potential is six dimensional, however, our tests of 4MR and 5MR calculations demonstrate that the 4MR convergence for most energy levels discussed here is better than 1 cm^{-1}. See more details in the Results Section, where 4MR and 5MR results are presented.

In MM calculations, the number of basis function is restricted by the maximum excitation quanta on each mode, and the maximum sum of excitation quanta on all modes. In our calculation, 26 primitive harmonic-oscillator basis functions are included with 18 Gauss Hermite integration points for each mode. The maximum quanta for single mode are tested from 8 to 12, and we obtained the convergence within in 0.1 cm^{-1}. For $J > 0$, vibrational basis is coupled with a rotational basis, and a detailed description can be found in references 14–16.

III. RESULTS

The equilibrium structure, rotational constants, and the harmonic frequencies of the cyclic C_4 are listed in Table I. The definition of structural parameters in this paper are consistent with that in Ref. 11.[2,11] As shown in Table I, our CCSD(T)-F12b/aVTZ structure is very similar to the CCSD(T)/pVQZ structure in Ref. 11. However, R_{12} and R_{13} from a previous MRCI+Q study[12] are longer than the CCSD(T)/CV5Z values by 0.007 Å and 0.015 Å, respectively. It is not unusual to see MRCI calculations overestimate the bond lengths and its deviations are mainly caused by the *ab initio* method limitations (compared to the error compensation in the CCSD(T) method), basis set incompleteness and the core correlation effects. Such structural deviations consequently lead to the large deviations in the MRCI vibrational frequencies. The harmonic frequency differences between the CCSD(T)-F12b/aVTZ PES and the CV5Z QFF are 2-10 cm^{-1}; these relatively small differences are reasonable considering the *ab initio* method and basis differences. The QFF harmonic frequencies are typically a little higher than the PES values, and this is a result of including core-correlation in the QFF calculation but not in the PES computations. The

CV5Z QFF force constants are tabulated in Table II.

The computed fundamental frequencies of $^{12}C_4$ using the PES and QFF with both VPT2 and VCI are presented in Table III. In addition, the IR intensities are estimated using the standard double-harmonic approximation using MP2/aVQZ theory. The results are 53.5, 29.9 and 203.2 km/mol for the three IR-active modes, which in the present notation are mode 4, 5, and 6, respectively. The MM-PES calculations are performed using both 4-mode representation (4MR) and 5-mode representation (5MR). The 4MR VCI results agree with 5MR to within 0.3 cm^{-1}. In addition, we test the convergence with respect to the number of the contracted basis functions and the allowed mode excitations. Less than 0.2 cm^{-1} differences are found for fundamentals, which clearly indicates the VCI basis convergence. In Table III, both VCI (MM-4MR) and VPT2 results are given for the CV5Z QFF. Agreement for the six vibrational fundamentals is 0 - 3 cm^{-1}, except ν_2 where the VPT2 energy is 7 cm^{-1} higher than the VCI energy. The ν_2 vibration is an in-plane breathing mode altering the bond angles within the original symmetry. The anharmonicity of the ν_2 fundamental increases by -4.4 cm^{-1} from -9.8 cm^{-1} (CVTZ) to -12.9 cm^{-1} (CVQZ) and -14.2 cm^{-1} (CV5Z), but the ν_2 harmonic frequency rises faster by 9.3 cm^{-1} from 940.3 cm^{-1} (CVTZ), 944.1 cm^{-1}(CVQZ) to 949.6 cm^{-1} (CV5Z). This suggests that convergence with respect to the one-particle basis set is reasonably good. The larger difference between VCI and VPT2 for the ν_2 fundamental suggests that second-order perturbation theory may not be as adequate for this particular mode, but the difference is still relatively small.

The VCI fundamental frequencies using the PES differ by less than 9 cm^{-1} compared to the VCI and VPT2 results using the QFF. The differences may partially result from the *ab initio* method, while they could also partially come from the fitting of the PES and QFF. Comparing the results in detail, we find that the harmonic frequency of the torsion mode ω_4 on the PES is about 7 cm^{-1} lower than that on the QFF, but the VCI ν_4 fundamentals are almost the same, 301.02 cm^{-1} (PES) vs. 300.62 cm^{-1} (QFF). Conversely, we see enlarged differences of mode 6 for which the harmonic frequency difference is 3.6 cm^{-1} while the MM fundamentals differ by 7.6 cm^{-1}. The PES vs. QFF harmonic frequency differences of the other 4 fundamentals are similar to their corresponding PES vs. QFF variational fundamentals. Comparing to previous studies, overall consistency with Martin's CCSD(T)

fundamentals is very good. By contrast, the results of the previous MRCI+Q QFF calculation have about 60 cm^{-1} deviations for some modes. They are mostly the result of the large differences in the MRCI+Q structure and harmonic frequencies (see Table I), which is mainly attributed to the *ab initio* method and basis limitations.

As noted already, Martin *et al.* reported the Fermi resonance $\nu_6 = \nu_3+\nu_5$ raises ν_6 by 9 cm^{-1}.[11] To investigate this, we examined the force constants in Table II. The off-diagonal cubic constant F_{653} is unusually large, 7.9852 aJ/Å^{2}rad. It leads to an exceptionally large k_{356} = -295.9 cm^{-1}. In off-diagonal quartic constants, F_{6531} is also unusually large, i.e. -20.2 aJ/Å^{3}rad, which leads to k_{1356} = -55.0 cm^{-1}. They are highly consistent with the two corresponding normal coordinate QFF constants reported in Ref. 11: -295.0 cm^{-1} and -54.8 cm^{-1}, respectively. This agreement confirms the consistency of both studies. Note that the k_{356} value quoted in the Ref. 11 text and introduction was actually for k_{166}. Combined together, they render significant anharmonicities for ν_6, i.e. 80 cm^{-1}. From the eigenvector analysis of the final VCI (MM) states, ν_6 is found to be strongly coupled with $\nu_3+\nu_5$. The $\nu_3+\nu_5$ CI basis contributes about 23% of the ν_6 fundamental wavefunction.

However, using the CV5Z QFF, the regular VPT2 ν_6 fundamental estimated without the explicit Fermi resonance $\nu_6 = \nu_3+\nu_5$ treatment is 1313.15 cm^{-1}, i.e. just 1.4 cm^{-1} lower than the value we report in Table III, which is estimated with explicit Fermi resonance treatment. The other component, $\nu_3 + \nu_5$, is 1.5 cm^{-1} higher, 1561.53 cm^{-1} (regular VPT2) vs. 1560.14 cm^{-1} (explicit Fermi resonance treatment), vs. 1555.15 cm^{-1} (MM-QFF 4MR). In addition, two more Fermi resonances (Type I) have been explicitly treated. Compared to VPT2 without including these resonances, ν_1 is reduced by 0.5 cm^{-1} and ν_2 is raised by 1.0 cm^{-1}. Therefore, all the Fermi resonance effects we observed using the CV5Z QFF fundamentals are smaller than those reported in Martin *et al.*. It is well known that the resonance effects can vary from one QFF to another.

Combination and overtone excitation energies of C_4 given in Table IV and are computed with regular VPT2, i.e., no explicit Fermi resonance treatment is included. For most energy levels the agreement between VCI (MM) and VPT2 results is within 10 cm^{-1}, with the VPT2 energies generally somewhat higher. For the states in Table IV where there are 3-5

cm^{-1} differences between MM and VPT2, the differences are totally consistent with the limitations of VPT2 treatment. There are only two exceptions: $\nu_3 + \nu_6$ and $\nu_5 + \nu_6$. For $\nu_3 + \nu_6$ and $\nu_5 + \nu_6$; the MM-QFF energies are higher than the VPT2-QFF energies by 13-20 cm^{-1}, while the VPT2-QFF energies agree well with the corresponding MM-PES energies. This could be accidental. For the MM-PES results, we obtain good agreement between the 4MR and 5MR results as well. Comparing MM-QFF to MM-PES, most differences are within 5 - 15 cm^{-1}. In addition, we note the strong coupling of $2\nu_6$ with $2\nu_3 + 2\nu_5$ and $\nu_6 + \nu_3 + \nu_5$. The MM calculations give two $2\nu_6$ states separated by about 200 cm^{-1}, as shown in Table IV. The leading CI coefficients in both $2\nu_6$ states are about 0.67. In this situation, assignment of $2\nu_6$ becomes problematic due to the severe mixing, and the labels are considered somewhat arbitrary.

In addition to the vibrational frequencies, vibrationally averaged structure, vibration-rotation interaction constants and rotational constants of cyclic C_4 are obtained using VPT2 and the results are given in Table V. The zero-point averaged values of R_{12} and R_{13} are longer than their equilibrium values by 0.0055 Åand 0.0081 Å, respectively. The zero-point averaged rotational constants are smaller than A_e, B_e, and C_e by 0.0075 cm^{-1}, 0.0019 cm^{-1}, and 0.0020 cm^{-1}, respectively. The MRCI+Q/pVTZ rotational constants reported in Ref.12 and given in Table V are almost certainly less accurate than the present ones owing to the higher accuracy of the present *ab initio* methods. For quartic centrifugal distortion constants, agreement between our CV5Z QFF and Ref.12 is just qualitative, with the present d_J and d_K smaller by one order of magnitude. From the VPT2 calculations, when vibration-rotation terms are taken into account, the A_v, B_v and C_v values vary by 0.01-0.02 cm^{-1} for the ν=1 states. Details can be found in the supplementary material (SM)[34].

We also obtain ro-vibrational energies of cyclic C_4 from the MM and the SPECTRO calculations. The ro-vibrational energies of the $J = 1$ and $J = 2$ levels computed with the MM-PES and VPT2-QFF approaches are given in Table VI, where we give $E_\nu(J = 1, 2) - E_\nu(J = 0)$. In addition to spectroscopic constants, SPECTRO also computes the ro-vibrational energy levels through diagonalizing the rotational energy matrices for both S and A reduced Hamiltonians. The vibrationally-dependent spectroscopic constants can be found in the SM. Note

the differences between S-reduced and A-reduced Hamiltonian energy matrices are much smaller than 1.0E-06 cm^{-1}, so we do not need to label them. The MM ro-vibrational energies calculation are obtained by diagonalizing the full ro-vibrational Watson Hamiltonian matrices with the nMR potential representation. Cyclic C_4 is not a rigid symmetric top, so there is no exact expression that relates the ro-vibrational energies of MM with the effective rotational constants. However, we use an approximate expression to represent the energy levels of the asymmetric rigid rotor is given by[35]:

$$E = \frac{1}{2}(A + C)J(J + 1) + \frac{1}{2}(A - C)E_\tau$$

where E_τ is tabulated according to the asymmetry parameter κ, which is defined as $(2B - A - C)/(A - C)$. κ is equal to about -0.72 for cyclic C_4, and the values of E_τ can be found in Ref. 35. According to this expression, effective A and C can be calculated through linear least squares fitting from the MM-PES ro-vibrational energies. Here if the effective rotational constants from SPECTRO are substituted into this expression to calculate the ro-vibrational energies, good consistency can be obtained comparing with the MM-PES energies, with differences less than 0.4 cm^{-1}. The differences are partly due to the simple approximation in the formula, they are also traced to differences in the equilibrium structures between the QFF and PES.

Finally, we consider two cyclic C_4 isotopologues. The MM and SPECTRO results for the two single ^{13}C-substituted isotopologues are shown in Table VII, including the zero-point structure, 6 vibrational fundamentals, and vibrationally averaged rotational constants. Additional VPT2 analyses for all other possible ^{13}C isotopologues are available in the SM. As seen in Table VII, good consistency is found between the three approaches for both isotopologues. We expect similar consistency for the fundamentals. The VPT2/QFF isotopic shifts are explicitly included as it is usually more accurate than the absolute values of fundamental frequencies. Compared to $^{12}C_4$, the shifts are relatively small for the bend and torsion modes, decreasing by less than 5 cm^{-1}. For the stretching modes, for example mode ν_1 and ν_6, the differences can be as large as about 14 cm^{-1} for the single ^{13}C isotopologues. Note the same Fermi resonance treatments are included in the VPT2 analysis on both isotopologues, although their effects are small, i.e. about 1 cm^{-1}.

IV. SUMMARY AND CONCLUSIONS

We reported a CCSD(T)-F12b/aug-cc-pVTZ potential energy surface and a CCSD(T)/cc-pCV5Z quartic force field for the singlet cyclic C_4. Three different methods were adopted to calculate the vibrational states of cyclic C_4: variational calculations (VCI) using MULTIMODE with the PES and the QFF, and second-order perturbation calculation using SPECTRO with the QFF. Even though the PES and QFF were constructed using different *ab initio* methods and basis sets, the VCI calculations using the PES and QFF are in very good agreement with each other for fundamentals, overtones, and combinations. On the CV5Z QFF, the VPT2 fundamentals agree excellently with the variationally calculated energies. From the VCI calculations, the coupling between the mode ν_6 and $\nu_3 + \nu_5$ combination is quite strong, but the VPT2 calculations with the Fermi resonance treatment explicitly included only change the ν_6 fundamental by 1.4 cm^{-1}. The other two Fermi resonance effects are less than 1 cm^{-1}. Ro-vibrational energies for $J = 1$ and $J = 2$ were reported from MM calculations on the PES and VPT2 calculations with the QFF. Spectroscopic constants including vibrationally averaged structures were determined by the VPT2 method and reported for the main isotopologue as well as two ^{13}C singly-substituted isotopologues. The accuracy of vibrational fundamentals is estimated to be better than 5 cm^{-1}. Rotational constant are estimated to be accurate to within 0.1-0.5% and quartic centrifugal distortion constants are estimated to be accurate to within 5-10%. The results reported in this study may help identification of cyclic C_4 in future experimental analyses or astronomical observations.

The PES and QFF are available upon request.

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[34]*See Supplementary Material Document at — for spectroscopic parameters of the cyclic C_4, and the ro-vibration energies with $J = 1$ and $J = 2$ of the cyclic C_4 isotopes.*

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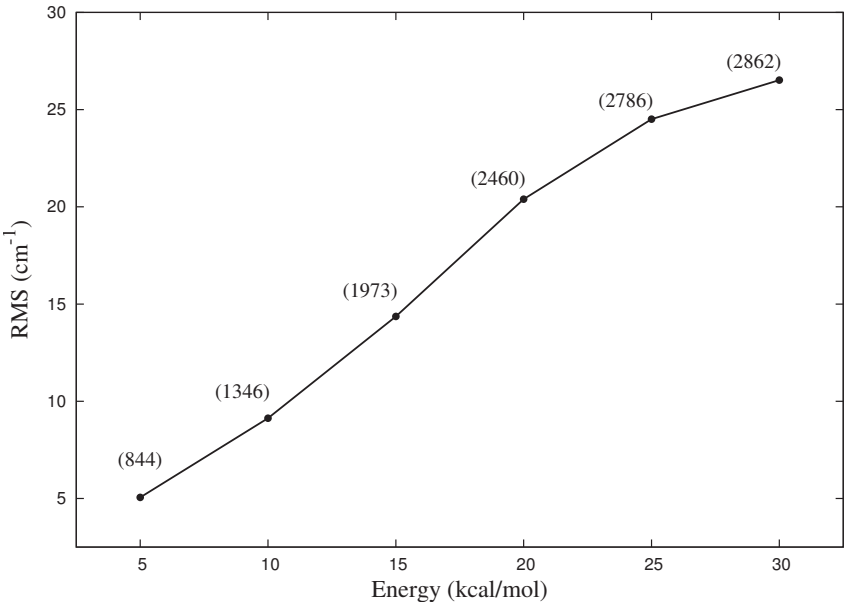

FIG. 1. Root-mean-square (RMS) of the PES fitting error vs. relative energy with respect to cyclic C_4 minimum. The numbers in parenthesis are the number of configurations in the energy range.

TABLE I. Computed equilibrium geometries (Å), rotational constants (cm^{-1}), and harmonic frequencies (cm^{-1}) of cyclic C_4 from the PES and *ab initio* calculations.

	PES	CCSD(T)-F12b	QFF	Ref.	
		/aVTZ	CV5Z	CCSD(T)[a]	MRCI[b]
Equilibrium geometires					
R_{12}	1.4481	1.4494	1.4439	1.4492	1.4510
R_{13}	1.5121	1.5110	1.5057	1.5125	1.5204
A_e	1.2277	1.2295	1.2383		1.2149
B_e	0.4599	0.4586	0.4623		0.4599
C_e	0.3346	0.3345	0.3366		0.3336
Harmonic frequencies					
ZPE	2736.8	2730.5	2751.3	2731.4	2815.9
$\omega_1(a_g)$	1267.9	1264.3	1272.2	1262.7	1306.6
$\omega_2(a_g)$	947.4	942.5	949.6	944.2	989.5
$\omega_3(b_{1g})$	1029.4	1030.8	1038.9	1030.8	1079.1
$\omega_4(b_{1u})$	299.4	301.4	306.1	304.7	284.3
$\omega_5(b_{2u})$	537.1	534.3	539.9	534.5	523.1
$\omega_6(b_{3u})$	1392.3	1386.6	1396.0	1385.9	1449.2

[a] Ref. 11 CCSD(T)/pVQZ calculation

[b] Ref. 12 MRCI+Q/pVTZ calculation

TABLE II. CCSD(T)/CV5Z QFF force constants in symmetry coordinates of cyclic C_4. Coordinates 1-6 follow the definitions in Ref. 11. All force constants are given in aJ/Å$^n \cdot rad^m$ where n and m are the orders of bond length coordinates and angle-related coordinates.

ij	F_{ij}	ij	F_{ij}	ij	F_{ij}
11	5.513082	21	-0.503134	22	1.770448
33	0.737645	44	0.068348	55	3.815147
66	4.730368				

ijk	F_{ijk}	ijk	F_{ijk}	ijk	F_{ijk}
111	-15.6237	211	1.1212	221	-3.3525
222	3.5236	331	-3.9763	332	-1.7894
441	-0.1205	442	0.3723	551	-14.2755
552	0.6873	653	7.9852	661	-14.6209
662	0.2381				

$ijkl$	F_{ijkl}	$ijkl$	F_{ijkl}	$ijkl$	F_{ijkl}
1111	36.18	2111	-2.42	2211	6.02
2221	-10.21	2222	15.92	3311	5.94
3321	4.70	3322	1.04	3333	10.55
4411	0.20	4421	-0.89	4422	0.19
4433	-0.37	4444	0.43	5511	37.77
5521	0.16	5522	-5.64	5533	10.68
5544	-0.47	5555	41.66	6531	-20.20
6532	-4.32	6611	35.92	6621	-0.29
6622	0.82	6633	9.45	6644	-0.20
6655	40.01	6666	29.57		

TABLE III. Computed zero-point energy (ZPE) and fundamentals (cm^{-1}) of cyclic $^{12}C_4$ using different methods

	Harm.	MM-PES		Harm.	MM-4MR	VPT2	Refs.		
	PES	4MR	5MR	QFF	QFF	QFF	CCSD(T)[a]	CCSD(T)[b]	MRCI[c]
ZPE	2736.84	2716.37	2716.36	2751.34	2729.76	2726.35	2713.6	2698.1	
$\nu_1(a_g)$	1267.88	1250.26	1250.26	1272.25	1256.66	1256.36	1248.6	1241.4	1285.9
$\nu_2(a_g)$	947.39	928.32	928.24	949.60	928.62	935.44	926.9	920.7	949.4
$\nu_3(b_{1g})$	1029.39	994.34	994.27	1038.85	1002.40	1002.93	998.7	989.3	981.5
$\nu_4(b_{1u})$	299.44	301.02	300.96	306.10	300.62	302.87	302.3	300.3	279.2
$\nu_5(b_{2u})$	537.15	520.86	520.81	539.91	520.59	522.60	520.2	511.6	522.5
$\nu_6(b_{3u})$	1392.33	1308.91	1308.64	1395.97	1316.57	1314.54	1313.5	1294.2	1378.0

[a] Ref. 11 CCSD(T)/pVTZ variational calculation

[b] Ref. 11 CCSD(T)/pVTZ perturbation calculation

[c] Ref. 12 MRCI+Q/pVTZ perturbation calculation

TABLE IV. Low-lying combinations and overtones of cyclic $^{12}C_4$ (cm^{-1})

Assignment	MM-PES		MM-QFF	VPT2-QFF
	4MR	5MR	4MR	
$2\nu_4$	606.69	606.58	603.21	608.67
$\nu_4 + \nu_5$	822.06	821.93	818.93	824.44
$2\nu_5$	1036.72	1036.61	1035.27	1037.84
$\nu_2 + \nu_4$	1232.92	1229.41	1225.84	1232.20
$\nu_3 + \nu_4$	1290.72	1290.48	1296.18	1299.06
$\nu_2 + \nu_5$	1439.13	1438.76	1435.14	1444.90
$\nu_3 + \nu_5$	1549.74	1549.66	1555.15	1561.52
$\nu_1 + \nu_4$	1556.93	1553.26	1559.61	1561.33
$\nu_6 + \nu_4$	1605.78	1604.97	1611.58	1611.72
$\nu_1 + \nu_5$	1773.20	1773.09	1779.88	1785.04
$\nu_6 + \nu_5$	1787.13	1786.16	1797.19	1784.11
$2\nu_2$	1853.43	1853.11	1855.11	1861.14
$\nu_3 + \nu_2$	1918.21	1918.01	1925.05	1923.23
$2\nu_3$	1984.99	1984.69	2000.95	2003.75
$\nu_1 + \nu_2$	2176.93	2173.39	2183.01	2184.35
$\nu_2 + \nu_6$	2218.54	2216.13	2225.79	2234.58
$\nu_1 + \nu_3$	2232.38	2232.20	2245.38	2245.56
$\nu_3 + \nu_6$	2247.65	2246.83	2264.19	2244.26
$2\nu_1$	2495.22	2495.17	2508.59	2508.82
$\nu_1 + \nu_6$	2547.08	2546.36	2561.28	2560.05
$2\nu_6$ [1]	2589.08	2587.19	2607.76	2617.20
$2\nu_6$ [2]	2794.38	2793.19	2810.37	

[1] Lower energy component of ν_6 overtone

[2] Higher energy component of ν_6 overtone

TABLE V. VPT2 vibrationally averaged structure (Å), vibration-rotation coupling constants (10^{-3} cm^{-1}), rotational constants (cm^{-1}) and centrifugal distortion constants (10^{-6} cm^{-1}) of cyclic C_4, in the Watson A reduced Hamiltonian.

	Zero-point	Ref.[a]	Vib-rot constants			
R_{12}	1.4494		Mode	α^A	α^B	α^C
R_{13}	1.5138		1	5.25	0.92	0.76
A_0	1.2308	1.2178	2	2.71	-0.37	0.66*
B_0	0.4604	0.4570	3	2.70	1.51	1.82*
C_0	0.3346	0.3319	4	29.64	-1.01	-1.38
D_J	0.2267	0.2129	5	-28.30	1.85	1.66
D_{JK}	0.7299	0.6571	6	5.16	1.53	1.11
D_K	5.4165	4.5530				
d_J	0.0630	0.592				
d_K	0.7992	7.157				

* means the values are affected by Coriolis resonance

[a] Ref. 12 MRCI+Q/pVTZ calculation

TABLE VI. Ro-vibrational energies of $J = 1$ and $J = 2$ from 4MR MM calculation with the PES and VPT2 calculation with the QFF, and the energies are shown as $\nu_{i(J=1,2)} - \nu_{i(J=0)}$. ($cm^{-1}$)

		$1_{1,0}$	$1_{1,1}$	$1_{0,1}$	$2_{2,0}$	$2_{2,1}$	$2_{1,1}$	$2_{1,2}$	$2_{0,2}$
MM	ZPE	1.6701	1.5449	0.7898	5.6533	5.6400	3.3748	2.9994	2.3561
	ν_1	1.6668	1.5412	0.7872	5.6462	5.6318	3.3686	2.9909	2.3479
	ν_2	1.6670	1.5405	0.7884	5.6421	5.6285	3.3707	2.9914	2.3515
	ν_3	1.6661	1.5395	0.7857	5.6422	5.6280	3.3652	2.9853	2.3435
	ν_4	1.6674	1.5426	0.7920	5.6366	5.6278	3.3760	3.0017	2.3670
	ν_5	1.5919	1.4675	0.7866	5.3521	5.3376	3.2907	2.9176	2.3454
	ν_6	1.6578	1.5327	0.7861	5.6165	5.5995	3.3588	2.9817	2.3432
VPT2	ZPE	1.6912	1.5653	0.7950	5.7321	5.7179	3.4071	3.0295	2.3708
	ν_1	1.6850	1.5593	0.7933	5.7095	5.6953	3.3974	3.0203	2.3658
	ν_2	1.6889	1.5620	0.7947	5.7213	5.7068	3.4052	3.0245	2.3697
	ν_3	1.6870	1.5608	0.7917	5.7181	5.7038	3.3965	3.0180	2.3608
	ν_4	1.6626	1.5371	0.7974	5.6164	5.6018	3.3829	3.0064	2.3776
	ν_5	1.7177	1.5920	0.7915	5.8413	5.8276	3.4263	3.0493	2.3609
	ν_6	1.6845	1.5591	0.7924	5.7088	5.6947	3.3949	3.0184	2.3630

TABLE VII. The VPT2 zero-point vibrationally averaged structures (Å, deg), rotational constants (cm^{-1}), zero-point energy (ZPE) (cm^{-1}), fundamentals (cm^{-1}) of single ^{13}C isotope substituted cyclic C_4, and shifts of vibration energies comparing with $^{12}C_4$ based on VPT2 results.

	Zero-point		Vibrational Energies					Shift
				Harm-QFF	MM-PES	MM-QFF	VPT2-QFF	
^{13}CCCC	R_{12}=R_{14}	1.4492	ZPE	2721.98	2687.64	2699.84	2697.62	-28.73
	R_{23}=R_{34}	1.4494	ν_1	1258.93	1237.12	1243.34	1243.59	-12.77
	$\angle_{123}$	62.960	ν_2	941.08	920.77	920.37	922.18	-13.26
	A_0	1.1825	ν_3	1023.51	980.25	987.80	988.67	-14.26
	B_0	0.4605	ν_4	303.13	298.09	297.66	299.96	-2.91
	C_0	0.3309	ν_5	534.39	515.66	515.22	517.38	-5.22
			ν_6	1382.92	1296.76	1303.83	1302.39	-12.15
C^{13}CCC	R_{12}=R_{23}	1.4493	ZPE	2726.96	2692.60	2704.75	2702.47	-23.88
	R_{34}=R_{14}	1.4493	ν_1	1260.34	1238.56	1243.90	1244.33	-12.07
	$\angle_{143}$	62.965	ν_2	938.59	917.23	917.54	919.34	-10.77
	A_0	1.2308	ν_3	1033.43	989.33	996.97	997.88	-5.05
	B_0	0.4424	ν_4	303.13	298.10	297.67	299.98	-2.89
	C_0	0.3249	ν_5	534.60	515.96	515.50	517.67	-4.93
			ν_6	1383.82	1299.15	1306.24	1304.52	-10.02