

Is there evidence for detection of cyclic C₄ in IR spectra? An accurate *ab initio* computed quartic force field

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The quartic force field of cyclic C₄ has been computed using basis sets of *spdf* quality and augmented coupled cluster methods. The effect of core correlation and further basis set extension has been investigated. Vibrational energy levels have been obtained using perturbation theory and two different variational approaches. A severe Fermi resonance exists between the most intense vibration, ν_6 , and $\nu_3 + \nu_5$ through an exceptionally large $k_{356} = -258.2 \text{ cm}^{-1}$; a large $k_{1356} = -54.8 \text{ cm}^{-1}$ causes significant higher-order anharmonicity, including a shift in ν_6 of $+9 \text{ cm}^{-1}$. C₄ appears to be an excellent test case for methods for solving the vibrational Schrödinger equation, since perturbation theory breaks down even when the above resonances are accounted for. Our best estimate for ν_6 , $1320 \pm 10 \text{ cm}^{-1}$, may suggest its assignment to a feature detected at 1284 cm^{-1} in argon and 1302 cm^{-1} in krypton matrix, but this would imply an unusually large matrix red shift in argon. © 1996 American Institute of Physics. [S0021-9606(96)03710-1]

I. INTRODUCTION

One long-standing point of controversy in carbon cluster chemistry (see Refs. 1 and 2 and the introduction to Ref. 3 for reviews) has been the structure of C_{2n} clusters. For C₄,⁴ C₆,^{5,6} and C₈,⁷ it has been well known for some time that linear $^3\Sigma_g^-$ states and monocyclic singlet ring structures are energetically competitive. While the linear structures for C₄ (Ref. 8) and C₆ (Ref. 9) have been detected in the infrared, the corresponding cyclic structures have always eluded detection, although Martin and Taylor⁷ suggest the presence of cyclic C₆ and possibly C₈ in infrared spectra of argon-trapped graphite vapor.^{10,11}

Nevertheless, Coulomb explosion¹² and electron photodetachment¹³ experiments definitely suggest the existence of a rhombic C₄ isomer. In previous *ab initio* work on the vibrational spectra of carbon clusters, Martin *et al.* suggested^{14,15} that an unassigned absorption at 1284 cm^{-1} (in argon matrix) belongs to cyclic C₄. However, they computed the harmonic frequencies at rather low levels of theory (such as MP2/6-311G*), and a recent coupled-cluster study with *spdf* basis sets⁴ predicted a harmonic frequency for the most intense band of about 1400 cm^{-1} .

At first sight this would preclude an assignment to the 1284 cm^{-1} band. However, given the peculiar structure of the rhombic form (which consists essentially of two fused C₃ rings), it is not inconceivable that anharmonicity would actually be on the order of 100 cm^{-1} . Of course it is hard to assess this without performing an anharmonic force field calculation at a sufficiently high level of theory. As we have shown in an extensive series of papers (Ref. 16 and references therein), reproduction or prediction of fundamentals to

better than 10 cm^{-1} is quite feasible using present-day methods. Therefore, such a study on cyclic C₄ is reported in the present communication, and would be expected to resolve the debate on whether or not cyclic C₄ has been observed in the infrared.

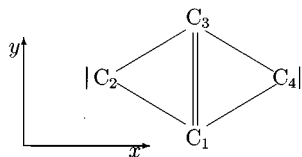
II. COMPUTATIONAL METHODS

All calculations were performed using Dunning's correlation consistent basis sets,¹⁷ which are denoted cc-pVnZ, i.e., correlation consistent polarized *n*-tuple zeta, where *n*=D for double, T for triple, and Q for quadruple zeta. The cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets are [3*s*2*p*1*d*], [4*s*3*p*2*d*1*f*], and [5*s*4*p*3*d*2*f*1*g*] contractions of (9*s*4*p*1*d*), (10*s*5*p*2*d*1*f*), and (12*s*6*p*3*d*2*f*1*g*) primitive sets, respectively. Core correlation effects were investigated using Dunning's cc-pCVTZ (correlation consistent polarized core-correlation valence triple zeta) basis set,¹⁸ which consists of the cc-pVTZ basis set augmented with (2*s*2*p*2*d*) high-exponent functions.

The CCSD(T) (Ref. 19) electron correlation method was used throughout. The acronym stands for coupled cluster with all single and double substitutions (CCSD) (Ref. 20) augmented with a quasiperturbative treatment of connected triple excitations.¹⁹ Extensive applications²¹ have shown this method to yield results that are consistently very close to full configuration interaction if nondynamical correlation effects are not overly important, that is, if the \mathcal{T}_1 diagnostic²² is not too large. Unless indicated otherwise, the (1*s*)-like core orbitals were constrained to be doubly occupied in all calculations.

All calculations were carried out with a program system consisting of the SEWARD integral package,²³ the supermatrix, SCF, and transformation parts of MOLECULE/SWEDEN,²⁴ and the vectorized closed-shell coupled cluster energy code from TITAN.²⁵ These programs were run on the Cray C90 at San Diego Supercomputer Center.

The following symmetry coordinate definitions were used (numbering our atoms clockwise starting on the short diagonal with the equilibrium configuration in the xy plane and the x axis along the long diagonal):



$$S_1(a_g) = \frac{1}{2}(r_{12} + r_{23} + r_{34} + r_{14}), \quad (1)$$

$$S_2(a_g) = \frac{1}{2}(\theta_{412} - \theta_{123} + \theta_{234} - \theta_{341}), \quad (2)$$

$$S_3(b_{1g}) = \frac{1}{\sqrt{2}}(\theta_{412} - \theta_{234}), \quad (3)$$

$$S_4(b_{1u}) = \frac{1}{2}(\tau_{1234} - \tau_{2341} + \tau_{3412} - \tau_{4123}), \quad (4)$$

$$S_5(b_{2u}) = \frac{1}{2}(r_{12} - r_{23} + r_{34} - r_{14}), \quad (5)$$

$$S_6(b_{3u}) = \frac{1}{2}(r_{12} + r_{23} - r_{34} - r_{14}), \quad (6)$$

in which r_{AB} represents the AB bond distance, θ_{ABC} the ABC bond angle, and τ_{ABCD} the angle between the ABC and BCD planes, respectively. Our potential expansion has the form:

$$V = \frac{1}{2} \sum_{ij} F_{ij} \Delta S_i \Delta S_j + \frac{1}{6} \sum_{ijk} F_{ijk} \Delta S_i \Delta S_j \Delta S_k + \frac{1}{24} \sum_{ijkl} F_{ijkl} \Delta S_i \Delta S_j \Delta S_k \Delta S_l, \quad (7)$$

where ΔS_i is the displacement from equilibrium.

A grid required to determine all nonvanishing quadratic, cubic, and quartic force constants by recursively applying the central difference approximation to the first derivative was then set up, with step sizes 0.01 Å or radian. This required 116 points in all, of which 41 are in D_{2h} symmetry, 56 in subgroups with order four, and 19 in subgroups with order 2. CCSD(T)/cc-pVTZ calculations were run for each of these, and the energies converged to essentially machine precision. The force constants were then calculated by finite differences of energies.

The one-particle basis set convergence was gauged by performing additional harmonic frequency calculations at the

TABLE I. Behavior of D_{2h} irreducible representations under the generators of the permutation inversion group used in this work.

D_{2h}	P_{13}	P_{24}	Parity
A_g	+	+	+
B_{1g}	-	-	+
B_{2g}	-	+	-
B_{3g}	+	-	-
A_u	+	+	-
B_{1u}	-	-	-
B_{2u}	-	+	+
B_{3u}	+	-	+

CCSD(T) level using the cc-pVDZ and cc-pVQZ basis sets. In addition, the effect of core correlation on the geometry and harmonic frequencies was explored by running CCSD(T)/cc-pCVTZ calculations in which all electrons were correlated.

We will estimate the effects of expanding the one-electron basis or including core correlation on the (anharmonic) vibrational energy levels by merging the CCSD(T)/cc-pVTZ quartic force field with a quadratic force field computed at a higher level of theory. The merging is performed by simply replacing the quadratic force constants and equilibrium geometry parameters.

The force field was then transformed to normal coordinates and a spectroscopic analysis carried out using both second order perturbation theory with the SPECTRO program²⁶ and the variational principle with the POLYMODE program^{27,28} ported to an IBM RS/6000. The POLYMODE program uses an approximation to the kinetic energy operator of the Watson²⁹ Hamiltonian, thus the computed energies will not be exact. These calculations used a basis of vibrational SCF (Ref. 27 oscillator products, with vibrational quantum numbers 0–6 in all in-plane modes, 0–8 in the out of plane mode, and with a maximum total quantum number of 8. This appears to give energies converged to better than 0.5 cm^{-1} .

Additional variational calculations were carried out using an exact kinetic energy operator. These used the procedures described elsewhere.³⁰ The details specific to the present system are as follows. The internal coordinates were based on the Jacobi vector connecting atoms 1 and 3 (\mathbf{R}_1) and the two Radau vectors relating atoms 2 and 4 to the center of mass of atoms 1 and 2 (\mathbf{R}_2 , and \mathbf{R}_3), i.e. CC+C+C in the notation of Ref. 30. The calculations are carried out using the ljk (Ref. 30) angular functions with the body fixed z axis along \mathbf{R}_1 . These coordinates enable one to take full advantage of the feasible permutations of the identical atoms; in Table I we give the behavior of the D_{2h} point group irreducible representations under the generators of the appropriate permutation-inversion group. To evaluate the potential energy matrix elements, the potential was re-expanded in the form

$$V = \sum_{ijklmn} C_{ijklmn} (R_1 - R_{1,e})^i (R_2 - R_{2,e})^j (R_3 - R_{3,e})^k \times \cos^{l-n} \tilde{\theta}_2 \cos^{m-n} \tilde{\theta}_3 \sin^n \tilde{\theta}_2 \sin^n \tilde{\theta}_3 \cos(n \tilde{\phi}_3), \quad (8)$$

TABLE II. Computed geometries (Å) and harmonic frequencies (cm^{-1}) of cyclic $^{12}C_4$.

	CCSD(T) cc-pVDZ valence (this work)	CCSD(T) cc-pVTZ valence (this work)	CCSD(T) cc-pVQZ valence (this work)	CCSD(T) cc-pCVTZ all e^- (this work)	CCSD(T) cc-pVTZ all e^{-a}	B3LYP/ cc-pVDZ ^b
r_{12}	1.4709	1.4540	1.4492	1.4497	1.442	1.4544
r_{13}	1.5388	1.5186	1.5125	1.5122	1.502	1.5081
$\omega_1(a_g)$	1256.6	1256.9	1262.7	1262.6	1279	1293
$\omega_2(a_g)$	927.2	938.8	944.2	944.2	956	945
$\omega_3(b_{1g})$	1018.1	1024.3	1030.8	...	1050	1019
$\omega_4(b_{1u})$	303.4	303.2	304.7	...	306(47.5)	300(46)
$\omega_5(b_{2u})$	535.6	527.7	534.5	...	532(50.2)	510(49)
$\omega_6(b_{3u})$	1374.4	1380.6	1385.9	1385.8	1405(259.6)	1397(249)

^aReference 4. All electrons correlated and Cartesian d, f functions used. The former causes significant differences since the cc-pVTZ basis set is only minimal in the core orbitals. IR intensities in km/mol given in parentheses.

^bReference 33.

where $i + j + k + l + m \leq 4$, $l + m$ is even, R_i , $\tilde{\theta}_i$, and $\tilde{\phi}_i$ are the spherical polar coordinates of \mathbf{R}_i in the body fixed frame, $R_{i,e}$ are equilibrium values, and the coefficients C_{ijklmn} were determined by numerically projecting out each $\cos(n\tilde{\phi}_3)$ component of Eq. (7) and matching up to fourth derivatives with respect to the remaining coordinates. Equation (7) cannot be used directly because it does not give a potential that behaves physically at all the limits of the angular coordinates. We used parameters which gave convergence to better than 0.1 cm^{-1} for low lying levels. This deteriorates to about 1 cm^{-1} for the highest levels given in this work.

III. RESULTS AND DISCUSSION

Computed equilibrium geometries and harmonic frequencies for $^{12}C_4$ are given in Table II. Computed fundamentals using different approaches are presented in Table III, while a list of low-lying vibrational levels of $^{12}C_4$ is given in Table IV. Finally, the complete quartic force field as defined in Eq. (7), can be found in Table V, both in terms of the symmetry-adapted internal coordinates defined by Eqs. (1)–(6) and of dimensionless normal coordinates.

Extending the basis set from cc-pVTZ to cc-pVQZ has a fairly significant effect on the computed geometry (Table II);

as a matter of fact, it is substantially larger than what would be expected from the empirical corrections proposed by Martin.³¹ It is not unexpected that a system as strained as cyclic C_4 would exhibit an unusually large basis set effect on the geometry. The effect on the harmonic frequencies is fairly small.

While an accurate treatment of core correlation would require basis sets well beyond what is feasible for this system, Martin³² has shown that the fairly small cc-pCVTZ basis set of Woon and Dunning¹⁸ recovers about three-quarters of the effect at fairly modest computational expense. As seen in Table II, the effects on both geometry and harmonic frequencies are of the same magnitude as those of extending the basis set from cc-pVTZ to cc-pVQZ. It is much smaller than the difference between our valence-only CCSD(T)/cc-pVTZ results and the all-electron CCSD(T)/cc-pVTZ results of Bartlett and coworkers;⁴ this reflects the well-known fact (see, e.g., Ref. 32) that basis sets that are minimal in the core tend to produce grossly exaggerated core correlation effects on geometries and especially harmonic frequencies.

TABLE III. Computed zero-point energy (ZPE) and fundamentals (cm^{-1}) of cyclic $^{12}C_4$ from the CCSD(T)/cc-pVTZ quartic force field using different methods.

Transition	Harmonic	Perturbation theory ^a	Variational calculations				
			Approximate kinetic energy ^b		Exact kinetic energy ^c		
ZPE	2715.8	2698.1	2695.9	2696.8	2696.3	2697.1	2713.6
$\nu_1(a_g)$	1256.9	1241.4	1241.4	1242.2	1241.4	1242.1	1248.6
$\nu_2(a_g)$	938.8	920.7	920.7	920.4	918.8	920.7	926.9
$\nu_3(b_{1g})$	1024.3	989.3	983.5	990.4	987.7	991.4	998.7
$\nu_4(b_{1u})$	303.2	300.3	300.3	299.0	299.4	299.8	302.3
$\nu_5(b_{2u})$	527.7	511.6	499.3	511.8	510.6	512.9	520.2
$\nu_6(b_{3u})$	1380.6	1294.2	1279.1	1302.5	1292.9	1304.9	1313.5
$\nu_3 + \nu_5(b_{3u})$	1552.0	1540.6	1519.5	1534.9	1534.3	1538.0	1550.5

^aCorrected for the $\omega_3 + \omega_5 \approx \omega_6$ resonance.

^bNeglecting all the k_{iii} , k_{ijk} , and k_{ijkl} .

^cUsing the cc-pVQZ quadratic force constants.

TABLE IV. Low-lying energy levels of cyclic $^{12}C_4$ (cm^{-1}).

Assignment	Absolute	Relative
	A_g	
000000)	2697.1	0.0
000200)	3299.4	602.3
010000)	3617.9	920.7
000020)	3718.7	1021.6
000400)	3910.5	1213.4
100000)	3939.3	1242.1
010200)	4216.9	1519.8
000220)	4319.6	1622.5
020000)?	4527.2	1830.1
100200)?	4536.6	1839.5
000600)?	4544.1	1847.0
010020)	4619.7	1922.6
002000)	4679.4	1982.3
000040)	4728.5	2031.4
	A_u	
001100)	3982.1	1285.0
001300)	4577.3	1880.2
000510)	4771.4	2074.3
	B_{1g}	
001000)	3688.6	991.4
001200)	4278.5	1581.4
000011)	4480.2	1783.1
011000)	4604.2	1907.1
001020)	4764.5	2067.4
	B_{1u}	
000100)	2997.0	299.8
000300)	3604.1	907.0
010100)	3915.9	1218.7
000120)	4017.8	1320.7
000500)	4218.4	1521.3
100100)	4240.3	1543.2
010300)	4520.5	1823.4
000320)	4623.9	1926.8
	B_{2g}	
000101)	4294.9	1597.8
001110)	4529.5	1832.4
	B_{2u}	
000010)	3210.0	512.9
000210)	3811.6	1114.5
010010)	4120.0	1422.9
000030)	4224.8	1527.7
000410)	4422.4	1725.3
100010)	4455.9	1758.8
010210)	4716.5	2019.4
	B_{3g}	
000110)	3509.5	812.3
000310)	4116.1	1419.0
010110)	4416.6	1719.5
000130)	4523.4	1826.3
100110)	4730.3	2033.2
100500)	4756.8	2059.7
	B_{3u}	
000001)	4002.1	1304.9
001010)	4235.1	1538.0
000201)	4590.8	1893.7

TABLE V. Quartic force field in symmetry coordinates and in dimensionless normal coordinates of cyclic C_4 . Units for symmetry coordinates are consistent with aJ for energy, Å for length, and radian for angles; all normal coordinate force constants are in cm^{-1} .

ij	F_{ij}	ϕ_{ij}	ij	F_{ij}	ϕ_{ij}
11	5.381 608 0	1256.9	21	-0.493 760 6	
22	1.754 337 2	938.8	33	0.715 421 7	1024.3
44	0.067 701 6	303.2	55	3.709 269 3	527.7
66	4.632 121 5	1380.6			
ijk	F_{ijk}	ϕ_{ijk}	ijk	F_{ijk}	ϕ_{ijk}
111	-15.256 45	-252.192	112	1.120 42	-24.539
122	-3.273 32	-143.606	133	-3.943 55	-249.166
144	-0.117 64	170.892	155	-13.812 86	-118.295
166	-14.258 61	-258.241	222	3.415 16	-48.355
233	-1.787 46	65.967	244	0.369 61	-136.334
255	0.666 61	96.233	266	0.267 90	69.495
356	7.838 02	294.995			
$ijkl$	F_{ijkl}	ϕ_{ijkl}	$ijkl$	F_{ijkl}	ϕ_{ijkl}
1111	34.840 49	45.098	1356	-19.713 03	-54.800
2111	-2.280 15	15.324	2211	5.831 60	36.154
2221	-9.900 11	31.859	2222	15.619 67	16.267
2365	-4.208 03	24.452	3311	5.998 14	39.627
3321	4.666 67	-19.658	3322	1.419 53	-16.336
3333	10.787 76	61.352	4411	0.202 21	-38.793
4421	-0.879 45	25.039	4422	0.201 33	-40.091
4433	-0.303 09	-65.801	4444	0.424 20	172.475
5511	36.206 83	10.672	5521	0.306 93	-20.332
5522	-5.250 88	12.882	5533	10.683 13	22.180
5544	-0.291 93	-40.577	5555	40.498 57	-9.119
6611	34.648 66	40.215	6621	-0.387 15	-11.058
6622	0.808 30	-10.339	6633	9.476 35	48.856
6644	-0.198 28	-71.280	6655	38.738 97	50.147
6666	28.135 19	28.169			

As expected, CCSD(T)/cc-pVDZ bond distances are seriously overestimated; somewhat surprisingly, for such a strained system, the harmonic frequencies are in very good agreement with those obtained using the cc-pVTZ or cc-pVQZ basis sets. This is encouraging for calculations on the larger cyclic carbon clusters,⁷ since CCSD(T)/cc-pVTZ frequency calculations on, say, C_{10} are simply not an option at the present time. The CCSD(T)/cc-pVDZ calculation also agrees well with density functional results³³ in the same basis set using the Becke 3-parameter-Lee-Yang-Parr (B3LYP) exchange-correlation functional.^{34,35}

Turning now to Table III, we find that the variational calculations using the approximate kinetic energy are in reasonable agreement with the accurate variational calculations, yielding fundamentals agreeing to within $1 cm^{-1}$, except for ν_6 , which is $2.5 cm^{-1}$ lower. The performance of perturbation theory, however, is not as good. Applying it without accounting for resonances yields reasonable values for the fundamentals ν_1 through ν_5 , but underestimates ν_6 by $11 cm^{-1}$. This is partially due to the existence of a severe Fermi type 2 resonance (with k_{356} equal to $-258.24 cm^{-1}$) between ω_6 and $\omega_3 + \omega_5$. Correcting for the resonance causes severe errors in both ν_5 and ν_6 , and less severely so in ν_3 .

TABLE VI. Absolute values of coefficients >0.05 of components of B_{3u} vibrational levels and shift (in cm^{-1}) due to introducing k_{1356} .

		Basis function							
Root	Energy	$ 000001\rangle$	$ 001010\rangle$	$ 010001\rangle$	$ 000021\rangle$	$ 011010\rangle$	$ 100001\rangle$	$ 001030\rangle$	$ 101010\rangle$
Including k_{iiii} and k_{ijij} only									
1	3989.2	0.851	0.504		0.086				
2	4230.9	0.519	0.827		0.157			0.062	
3	4883.8		0.144	0.685	0.384	0.444		0.322	0.057
4	4959.1		0.150	0.514	0.604	0.202	0.093	0.489	0.104
5	5145.8			0.485	0.220	0.807			
6	5220.8						0.828	0.086	0.488
7	5312.5			0.104	0.584	0.184	0.153	0.691	0.200
8	5470.9				0.105		0.503	0.237	0.780
Additionally including k_{1356}									
Root	Shift	$ 000001\rangle$	$ 001010\rangle$	$ 010001\rangle$	$ 000021\rangle$	$ 011010\rangle$	$ 100001\rangle$	$ 001030\rangle$	$ 101010\rangle$
1	+9.2	0.867	0.483		0.076				
2	+1.1	0.493	0.846		0.147			0.056	
3	+14.4		0.117	0.739	0.345	0.447		0.276	
4	+19.4		0.143	0.464	0.657	0.139	0.084	0.510	0.063
5	-0.6			0.456	0.234	0.821			
6	+12.4						0.848		0.475
7	-6.0			0.103	0.549	0.196	0.188	0.713	0.203
8	1.8				0.138		0.503	0.227	0.809

This performance is somewhat disconcerting, since we know from experience (e.g., Ref. 16) that second order perturbation theory—if the appropriate corrections are made—deals well with even multiple coupled Fermi resonances. The failure here suggests that yet another issue is involved.

Up to second order in perturbation theory, normal coordinate force constants of the types k_{iiij} , k_{iijk} , and k_{ijkl} do not contribute to the vibrational energies, while their effects are of course included in both sets of variational calculations. In order to assess their effect, we have repeated the variational calculations using the approximate kinetic energy operator with a potential from which these force constants are deleted. As seen in Table III, this results in energy levels quite similar to the uncorrected perturbation theory calculations. This means that some off-diagonal quartic force constant is responsible for a significant higher-order resonance, which has an indirect effect on ν_6 .

There are only eight such constants, and only three of these involve the mode of interest. Deleting the other five *en bloc* does not significantly alter the energy levels. By successively eliminating the other three, we find that most of the effect is caused by k_{1356} , which, at -54.8 cm^{-1} , is unusually large for an off-diagonal quartic constant. A detailed comparison of energy levels and expansion coefficients shows that at least eight states appear to be included in a resonance polyad: (see Table VI). Here, roots 1 and 2 are the partners in the Fermi type 2 resonance previously noted and, despite the fairly large separation of the zero-order states, the states mix in almost 2:1 ratios due to the very large k_{356} . Which of these interactions immediately involve k_{1356} ? Using the integrals of harmonic oscillator functions (Appendix 3 of Ref. 36) we find $|000001\rangle$ and $|101010\rangle$, $|001010\rangle$ and $|100001\rangle$, (each $k_{1356}/4$) and $|000021\rangle$ and $|101010\rangle$ ($k_{1356}/\sqrt{8}$). And indeed, the most noticeable change in ex-

pansion coefficients between the situations with and without k_{1356} occurs in root 4, particularly in the $|101010\rangle$ component. It would then be seductive to argue that root 8 causes a large perturbation in root 4, which in turn, through a cascade of k_{356} Fermi type 2 couplings, affects root 2 and then root 1.

However, a 2×2 eigensystem for roots 4 and 8 shows that the perturbation on root 4 would be on the order of 1 cm^{-1} , which is an order of magnitude lower than the effect we are trying to explain. A more telling observation is the fact that the largest shifts occur for those roots whose principal basis function involves mode 6—and a significant shift occurs for all roots involving modes 3, 5, or 6. Therefore, a more likely explanation for the effect of k_{1356} on the energy level series would be as a higher-order contribution to the anharmonicity.

We next repeated the above calculation, but with k_{356} set to zero. The effect of adding k_{1356} then was found to disappear almost entirely, which suggests the involvement of a higher-order contribution with the product of these force constants in the numerator. For a term involving the product of these two force constants to have a nonvanishing contribution to ν_6 at third order, the third constant should be k_{1ii} ($i = 1-6$). And indeed, leaving k_{1356} and k_{356} both in but zeroing out all k_{1ii} suppresses the effect as well. Upon successively reintroducing them, we find that $k_{166} = -129.12$ and $k_{133} = -124.59 \text{ cm}^{-1}$ each account for more than 40% of the effect, with a smaller contribution from $k_{155} = -59.15 \text{ cm}^{-1}$ and virtually all the remainder from $k_{111} = -126.10 \text{ cm}^{-1}$. Some algebraic manipulation reveals that, at third order in perturbation theory, the products $k_{356}k_{1356}k_{1aa}$ contribute to the second anharmonicity constants Y_{ijk} as well as to the small difference between effective and mechanical ω_i , but neither to E_0 nor to the X_{ij} . The

contribution of $k_{356}k_{1356}k_{166}$ to Y_{i66} ($i=1,3,5$) is of particular importance here.

It is now also easily understood why ν_5 and especially ν_3 were affected as well [particularly through Y_{i55} ($i=1,3,6$) and Y_{i33} ($i=1,5,6$), respectively], albeit to a lesser extent.

In a perturbation theory calculation with the $\nu_3 + \nu_5 \approx \nu_6$ Fermi resonance deleted we should consider higher-order terms to the effective Fermi resonance constant $K_{356} = \sqrt{8} \langle (\nu_6)^* | H | (\nu_3 + \nu_5)^* \rangle$. [The first-order term $K_{356}^{(1)} = k_{356}$.] The $k_{1356}k_{1ii}$ products are readily seen to contribute to K_{356} at second order, which will result in effects on $(\nu_6)^*$ and $(\nu_3 + \nu_5)^*$ starting at third order through the product $K_{356}^{(2)}k_{356}$.

Whether or not k_{2356} is included also seems to have a mild effect (+1.1 cm⁻¹ when included) on root 1. Pursuing a similar argument, we find this effect to come from third-order contributions involving $k_{356}k_{2356}k_{2ii}$. Not only is $k_{2356} = +24.45$ cm⁻¹ less than half the size of k_{1356} , but the k_{2ii} are appreciably smaller, the largest ones being $k_{244} = -68.17$ and $k_{255} = +48.12$ cm⁻¹, with $k_{233} = +32.99$ and $k_{266} = +34.75$ being still smaller. Under these circumstances, the much smaller magnitude of the perturbation is readily understood.

It is perhaps worth pointing out that inclusion of the constant E_0 term³⁷ in the perturbation theory calculations is found to be essential both to reproduce the variational zero-point energy, and to make it more or less stable under deleting Fermi-resonant interactions from the contact transformation. In the present case, $E_0 = 23.46$ cm⁻¹ if the $\nu_3 + \nu_5 \approx \nu_6$ resonance is not deleted from the contact transformation, and 5.41 cm⁻¹ if it is. The corrected zero-point energies differ by about 2 cm⁻¹, an order of magnitude less than the uncorrected ones. We have observed similar behavior in other molecules with strong Fermi resonances, e.g. H₂CO and C₂H₄.

If we include the more accurate cc-pVQZ harmonic force constants, the shift in the zero order levels is small; ω_6 goes up by 5.3 cm⁻¹, while the $\omega_3 + \omega_5$ combination goes up by 13.3 cm⁻¹. Since the gap widens slightly, the resonance perturbation will be smaller and the blue shift in ν_6 is expected to be somewhat larger than 5.3 cm⁻¹. And in fact, in Table III we do see a blue shift of 8.6 cm⁻¹.

In Table IV we give all the vibrational energy levels with energies less than about 4800 cm⁻¹ obtained with the variational calculations using the exact kinetic energy. Also given are labels for a separable approximation, determined from matching the energy levels with those computed using POLYMODE and identifying the component with the largest coefficient. In some cases, assignments become problematic due to the strong resonance mixing, and the labels must be considered somewhat arbitrary.

We can summarize by saying that basis set incompleteness and core correlation combined will increase ν_6 by about 10–15 cm⁻¹ above the CCSD(T)/cc-pVTZ value, which would correspond to a CCSD(T) limit value of 1315–1320 cm⁻¹. In order for this to correspond to the experimentally observed band at 1284 cm⁻¹, this would imply either a large

matrix red shift or significant deficiencies of the CCSD(T) electron correlation method. With a \mathcal{F}_1 diagnostic equal to 0.0155, the latter seems highly improbable. As for the former, a recent review by Jacox³⁸ indicates that a matrix shift of this magnitude in argon is not necessarily impossible, but high-resolution gas-phase measurements by the Saykally group³⁹ indicate that the matrix red shift of at least *linear* carbon clusters is more or less linearly related to the number of atoms, with a matrix shift of about 5 cm⁻¹ for C₄ and about 15 cm⁻¹ for C₉. While this would appear to make a matrix red shift of about 30 cm⁻¹ somewhat unlikely, it is not inconceivable that the behavior of cyclic C₄ is radically different in this regard, and the Jacox review contains several cases with matrix shifts in Ar of 30 cm⁻¹ or more. Moreover, from the work of Nachtigall,¹¹ it appears that the same feature seen at 1284 cm⁻¹ in an argon matrix shifts to 1302 cm⁻¹ in a krypton matrix. So there is a distinct possibility that the assignment by Martin *et al.*^{14,15,40} of the 1284 cm⁻¹ band to cyclic C₄ is correct, but it would imply an unusually large red shift in an argon matrix.

Furthermore, while there are several very weak features in the IR spectrum of argon-trapped carbon vapor¹⁰ between the 1284 and 1346 cm⁻¹ bands, it is far from certain that they correspond to anything other than background noise.

What we do obtain from our results is some indication of the anharmonicity to be expected for the larger rings. More than half of the 75.7 cm⁻¹ anharmonic correction found for the most intense band of C₄ is due to Fermi resonance perturbation: from the results in Table III, the harmonic frequencies, and k_{356} we find a deperturbed ν_6 of 1349.1 cm⁻¹, or an anharmonic contribution of -31.5 cm⁻¹. A conservative estimate for the effect of anharmonicity on the highest IR-active ring deformation of clusters like C₆, C₈, and C₁₀ would probably be on the order of -(50–100) cm⁻¹—provided no significant resonances perturb the band involved.

Finally, we give ¹²C:¹³C isotopic shifts on ν_6 for the isotopomers with D_{2h} symmetry. (For computational reasons, we were unable to treat the lower symmetry cases.) The isotopic bands are: ¹²C₄ 1304.9; ¹³C₂¹²C₂ 1279.8 and 1281.7 (with ¹³C atoms on short and long diagonal, respectively); and ¹³C₄ 1256.0 cm⁻¹. (Note the deviation of 2.4 cm⁻¹ from the Teller–Redlich rule in the final band.)

IV. CONCLUSIONS

The quartic force field of cyclic C₄ has been computed *ab initio* at the CCSD(T)/cc-pVTZ level and its vibrational energy levels computed using a variety of methods. The most intense band, ν_6 , is very significantly perturbed by a strong Fermi type 2 resonance $\nu_3 + \nu_5 \approx \nu_6$. In addition, a third-order contribution involving k_{1356} perturbs ν_6 by about 10 cm⁻¹. Due to these occurrences, cyclic C₄ is an excellent test case for methods for solving the vibrational Schrödinger equation. For this reason, we are making the quartic force field of C₄ available in Table V as well as on the World Wide Web at the Uniform Resource Locator (URL): <http://www.luc.ac.be/Research/TheoChem/Papers/C4.html>

Extending the basis set to cc-pVQZ and inclusion of core correlation both push the computed fundamentals upward. Our best estimate for ν_6 is $1320 \pm 10 \text{ cm}^{-1}$, which might be compatible with an assignment of the feature seen at 1284 cm^{-1} in Ar matrix and at 1302 cm^{-1} in Kr matrix, but would imply an unusually large matrix red shift in argon.

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