Fluorescence excitation and ultraviolet absorption spectra and theoretical calculations for benzocyclobutane: Vibrations and structure of its excited $S_1(\pi, \pi^*)$ electronic state

Hee Won Shin,¹ Esther J. Ocola,¹ Sunghwan Kim,² and Jaan Laane^{1,a)}

¹Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255, USA

²National Center for Biotechnology Information, National Library of Medicine, National Institutes of Health, Department of Health and Human Services, 8600 Rockville Pike, Bethesda, Maryland 20894, USA

(Received 21 October 2013; accepted 12 December 2013; published online 15 January 2014)

The fluorescence excitation spectra of jet-cooled benzocyclobutane have been recorded and together with its ultraviolet absorption spectra have been used to assign the vibrational frequencies for this molecule in its $S_1(\pi, \pi^*)$ electronic excited state. Theoretical calculations at the CASSCF(6,6)/aug-cc-pVTZ level of theory were carried out to compute the structure of the molecule in its excited state. The calculated structure was compared to that of the molecule in its electronic ground state as well as to the structures of related molecules in their S_0 and $S_1(\pi, \pi^*)$ electronic states. In each case the decreased π bonding in the electronic excited states results in longer carbon-carbon bonds in the benzene ring. The skeletal vibrational frequencies in the electronic excited state were readily assigned and these were compared to the ground state and to the frequencies of five similar molecules. The vibrational levels in both S_0 and $S_1(\pi, \pi^*)$ states were remarkably harmonic in contrast to the other bicyclic molecules. The decreases in the frequencies of the out-of-plane skeletal modes reflect the increased floppiness of these bicyclic molecules in their $S_1(\pi, \pi^*)$ excited state. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4858412>]

I. INTRODUCTION

In recent years we have investigated the structures, conformations, and molecular vibrations of bicyclic molecules in their ground and excited states. Among these are indan (IND),¹ tetralin (TET),² 1,4-benzodioxan (14BZD),³⁻⁵ 1,3-benzodioxan (13BZD),⁶ and 1,4-dihydronaphthalene (14DHN).⁷ In the present study we report our results on the $S_1(\pi, \pi^*)$ electronic excited state of benzocyclobutane (BCB) utilizing fluorescence excitation spectroscopy (FES) and ultraviolet absorption spectroscopy (Scheme 1). The vibrational study of the BCB S_0 ground state is reported in Ref. 8.

The focus of these studies has been not only to determine the structures and vibrational data for these molecules but also to understand what effect the $\pi \rightarrow \pi^*$ transition has on the rigidity and conformations of the molecules. Each of these molecules has a ring-flapping vibration whose frequency decreases dramatically in the $S_1(\pi, \pi^*)$ excited states. In addition, many of the vibrational frequencies and bond distances reflect the weakening of the π -bonding in the electronic excited states. The five-membered ring of indan (IND) is puckered with a barrier to planarity of 488 cm^{-1} (1.40 kcal/mole) in its S_0 ground state. This drops to 441 cm^{-1} (1.26 kcal/mole) in its excited state. The six-membered ring in tetralin (TET) is twisted with a barrier to planarity of about 6000 cm^{-1} (17 kcal/mole) in its S_0 electronic ground state and this drops to about 3500 cm^{-1} (10 kcal/mole) in its $S_1(\pi, \pi^*)$ state. For 1,4-benzodioxan (14BZD) the calculated twisting barrier values are 11.7 kcal/mole for the ground state

and 9.2 kcal/mole for the $S_1(\pi, \pi^*)$ excited state. 1,4-Dihydronaphthalene (14DHN) is planar and relatively floppy in its S_0 state but becomes even more so in its $S_1(\pi, \pi^*)$ state. Benzocyclobutane (BCB), the molecule of interest here, is expected to remain planar in both its S_0 and $S_1(\pi, \pi^*)$ states, but the difference in the rigidity of the molecule between the two electronic states as reflected by its out-of-plane vibrations will be the focus of the work. BCB has a highly strained four-membered ring attached to the benzene ring and what its effect is on the low-frequency vibrations will be investigated.

II. EXPERIMENTAL

The BCB sample (98% purity) was purchased from Aldrich Chemical Company and further purified by vacuum distillation. Ultraviolet absorption spectra of the vapor at ambient temperatures were recorded on a Bomem DA8.02 Fourier transform spectrometer using a deuterium

SCHEME 1. Bicyclic molecules of interest.

^{a)} Author to whom correspondence should be addressed. Electronic mail: laane@mail.chem.tamu.edu

lamp source, a quartz beamsplitter, and a silicon detector in the 20 000 to 50 000 cm^{-1} region. Approximately 3 Torr of sample was contained in a 20 cm glass cell with quartz windows. A resolution of 1 cm^{-1} was used and 4000 scans were averaged. The fluorescence excitation spectra (FES) were recorded using a Continuum Powerlite 9020 Nd:YAG laser which pumped a Continuum Sunlite optical parametric oscillator (OPO) and an FX-1 ultraviolet extension unit. The laser was scanned under computer control and the fluorescence was detected with a photomultiplier tube whenever resonance with a vibronic level was achieved. The FES were obtained at 0.5 cm^{-1} resolution and recorded under supersonic jet-cooled conditions. More details on the laser system are provided in Refs. 9–16.

III. COMPUTATIONS

In the present study, geometry optimizations and harmonic vibrational frequency computations for BCB in its lowest singlet excited state, $S_1(\pi, \pi^*)$, as well as in its ground state, were performed using the complete-active-space self-consistent-field (CASSCF) method with the aug-cc-pVTZ basis sets. The active space for the CASSCF computations consisted of six π electrons distributed in six π orbitals on the six-membered ring of BCB, as depicted in Figure 1. All CASSCF(6,6)/aug-cc-pVTZ computations were performed using the GAMESS program.^{17,18} A scaling factor of 0.905 was used for excited state calculated frequencies.¹⁹ The MacMolPlt²⁰ program was used to visualize the excited state vibrational motions of BCB.

FIG. 1. Molecular orbital diagram for the π and π^* orbitals of BCB.

We have previously reported our electronic ground state results for BCB.⁸ MP2/cc-pVTZ calculations were used to compute the structures of BCB and related molecules using the Gaussian 09 package.²¹ The geometrical parameters calculated in the present work for the BCB electronic ground state using the CASSCF method were very similar to the previous MP2/cc-pVTZ results.⁸ In the previous work B3LYP/cc-pVTZ calculations were utilized to compute the vibrational spectra and these were compared to the experimental vapor and liquid phase infrared and Raman spectra. Frequencies for the ground state below 1450 cm^{-1} were scaled with a factor of 0.985, frequencies in the 1450–2000 cm^{-1} region were scaled by a factor of 0.973, and frequencies above 2000 cm^{-1} by 0.961 based on previous work.^{22–26} The Semichem AMPAC/AGUI 9.2²⁷ along with the potential energy distribution (PED) was used to assign the vibrations for the electronic ground state.

In addition to the computational results reported here, we have also carried out CIS/6-311++G(d,p) calculations for the excited state of BCB. Since the calculated bond distances and angles did not differ significantly from our results from the CASSCF computations, the results are not presented here.

IV. STRUCTURES

Figure 2 shows the calculated structure of BCB for both its ground (S_0) and $S_1(\pi, \pi^*)$ excited states using the CASSCF(6,6)/aug-cc-pVTZ level. The determinants with the largest contributions to the CASSCF wave function for the $S_1(\pi, \pi^*)$ state of BCB correspond to excitation from the π_3 to π_4^* orbitals and from the π_2 to π_5^* orbitals. As a result, the electronic excitation from the S_0 to $S_1(\pi, \pi^*)$ states increases all the C–C bonds of the benzene ring. Note that the C–C bonds between the benzene ring and the CH_2 group are slightly shorter in the $S_1(\pi, \pi^*)$ state than in the ground state. This may be due to an increased hyperconjugative interaction between the C–H σ bonding orbitals on the methylene group and the half-filled π bonding orbitals.

Figure 3 shows the structures for both IND and TET with selected bond distances and angles from the MP2/cc-pVTZ calculations performed on the ground state.⁸ Selected bond distances and angles of IND¹ and TET² in their $S_1(\pi, \pi^*)$, electronic excited state are also shown. The calculations performed for IND in the excited state¹ utilized the CIS/6-31G(d) basis set, whereas the basis set used for the excited state calculations for TET² was CIS/6-311++G(d,p). Figure 1 presents a representation of the molecular orbitals of BCB so that the $\pi \rightarrow \pi^*$ electronic transition can be visualized. As discussed in Ref. 8, the structure for the ground state is quite typical for what is expected for a bicyclic molecule containing the benzene ring. Namely, the carbon-carbon bond distances are all 1.39 ± 0.01 Å for BCB as well as for IND and TET. The $\angle \text{C–C–C}$ angles in the benzene ring are all $120^\circ \pm 1^\circ$ for IND and TET, but the small ring angles of the four-membered ring in BCB cause the $\angle \text{C–C–C}$ angle at the carbon joined to the external ring to open up to 122° . In the $S_1(\pi, \pi^*)$ excited states, as expected, all of the C–C bonds in the benzene

FIG. 2. Calculated structures of BCB in its S_0 ground and $S_1(\pi,\pi^*)$ excited states (CASSCF(6,6)/aug-cc-pVTZ).

rings increase. For BCB they are 1.43 ± 0.01 Å reflecting an average increase of 0.03 Å. For IND they are 1.42 ± 0.02 Å with an increase of 0.02 Å and for TET they are 1.42 ± 0.01 Å, also with an increase of 0.02 Å. This shows that greater angle strain in the external ring of BCB results in somewhat

larger increases in the carbon-carbon bond lengths of the benzene ring. It is also interesting to note that the C-C bond from the benzene ring to an external carbon decreases slightly in the $S_1(\pi,\pi^*)$ excited state by 0.006 Å for BCB and by 0.009 Å for IND and TET.

FIG. 3. Calculated structures of IND and TET in their S_0 ground and $S_1(\pi,\pi^*)$ excited states. The S_0 structures were calculated using MP2/cc-pVTZ.⁸ The S_1 structure for IND¹ utilized CIS/6-31G(d). The S_1 structure for TET² utilized CIS/6-311++G(d,p).

FIG. 4. Fluorescence excitation spectrum and ultraviolet absorption spectrum of BCB. The 0_0^0 band origin is at $37\,093.6\text{ cm}^{-1}$.

V. RESULTS AND DISCUSSION

Figure 4 presents the fluorescence excitation spectrum (FES) of jet-cooled BCB and its ultraviolet (UV) absorption spectrum of BCB at room temperature in the -320 to 1700 cm^{-1} region, relative to the electronic band origin 0_0^0 at $37\,093.6\text{ cm}^{-1}$.

Table I compares the BCB electronic band origin to those of related molecules. The BCB transition frequency is the highest among these except for 13BZD which shows the effect of attaching an oxygen atom to the benzene ring. Figure 5 shows the UV spectrum expanded in the -340 to 25 cm^{-1} region. A number of assignments are shown in the Figures 4 and 5. Table II presents a summary of the vibrational assignments for the ground and excited states of BCB.

TABLE I. Observed electronic transition frequencies (cm^{-1}) and average calculated benzene ring bond distances ($\text{\AA}$) of BCB and related molecules.

	Transition frequency	Average benzene ring bond distance		Reference ^a
		S_0	$S_1(\pi, \pi^*)$	
BCB	37 093.6	1.395 ^b	1.429 ^c	This work
IND	36 903.7	1.395 ^b	1.416 ^d	1
TET	36 789.7	1.396 ^b	1.415 ^e	2
14BZD	35 563.1	1.391 ^b	1.419 ^e	3–5
13BZD	38 885.6	1.394 ^b	1.405 ^f	6
14DHN	36 788.6	1.393 ^b	...	7

^aReferences for transition frequencies and S_1 state bond distances. All S_0 state bond distances are from Ref. 8.

^bMP2/cc-pVTZ.

^cCASSCF(6,6)/aug-cc-pVTZ.

^dCIS/6-31G(d).

^eCIS/6-311++G(d,p).

^fCIS/6-311+G(d,p).

The ground state data were presented in Ref. 8 whereas the excited state data have been derived from Table III, which presents the experimental FES and UV absorption data for the most significant transitions. A more complete listing of the spectral data is available in Table S1 in the supplementary material.²⁸ Figure 6 presents an energy map for several of the low-frequency vibrations of BCB in its ground and excited electronic states. This energy map is consistent with the data and assignments of Table III. Table II also shows the calculated frequencies for both the S_0 and $S_1(\pi, \pi^*)$ states. As can be seen, these provide excellent guidance for assigning the experimental spectra. In order to allow comparison with the related molecules, Table IV shows a listing of selected vibrational frequencies of BCB, IND, TET, 14BZD, 13BZD, and 14DHN in their ground (S_0) and excited (S_1) states.

There are a number of noteworthy features regarding the BCB vibrations. The molecule is rigidly planar in its

FIG. 5. UV absorption spectra of BCB in the -340 to 21 cm^{-1} region. The 0_0^0 band origin is at $37\,093.6\text{ cm}^{-1}$.

TABLE II. Vibrational frequencies (cm^{-1}) of BCB in its ground and excited electronic states.

			S_0		$S_1(\pi, \pi^*)$	
			Experimental ^a	Calculated ^a	Experimental ^b	Calculated ^c
A ₁	ν_1^a	CH sym. stretch	3077	3061	3068	3045
	ν_2	CH sym. stretch	3052	3043	3015	3024
	ν_3	CH ₂ sym. stretch	2949	2928	2845	2876
	ν_4	Benzene C–C stretch	1605	1599	1643	1679
	ν_5	Benzene C–C stretch	1466	1461	1491	1484
	ν_6	CH ₂ deformation	1444	1440	1402	1454
	ν_7	Benzene C–C stretch ^d	1344	1345	1370	1360
	ν_8	CH wag ^d	1195	1203	1167	1170
	ν_9	CH ₂ wag ^d	1182	1189	1208	1209
	ν_{10}	CH wag	1152	1160	1113	1112
	ν_{11}	Benzene C–C stretch	1001	1009	892	843
	ν_{12}	4 mem. ring C–C stretch	895	893	900	868
	ν_{13}	4 mem. ring C–C stretch ^d	765	782	740	713
	ν_{14}	Benzene angle bend	539	542	464	465
A ₂	ν_{15}	CH ₂ antisym. stretch	2966	2957	...	2893
	ν_{16}	CH ₂ twist	1170	1169	1150	1169
	ν_{17}	CH ₂ rock	1054	1034	966	962
	ν_{18}	CH out-of-plane wag	993	981	656	635
	ν_{19}	CH out-of-plane wag	865	873	549	502
	ν_{20}	Benzene ring twist	670	710	440	450
	ν_{21}	Benzene ring twist	486	485	314	312
	ν_{22}	Skeletal twist	208	189	153	157
B ₁	ν_{23}	CH stretch	3066	3052	...	3039
	ν_{24}	CH stretch	3031	3035	...	3012
	ν_{25}	CH ₂ sym. stretch	2942	2923	...	2866
	ν_{26}	Benzene C–C stretch	1596	1593	1500	1502
	ν_{27}	Benzene C–C stretch	1458	1455	1364	1366
	ν_{28}	CH ₂ deformation	1429	1427	1426	1438
	ν_{29}	CH wag in-plane	1282	1292	1266	1261
	ν_{30}	CH ₂ wag	1208	1218	1188	1174
	ν_{31}	CH wag in-plane	1132	1138	972	972
	ν_{32}	4 mem. ring C–C stretch ^d	1091	1089	1085	1083
	ν_{33}	Benzene ring bend ^d	855	854	819	825
B ₂	ν_{34}	Benzene ring bend	634	637	564	567
	ν_{35}	Skeletal deformation	404	409	366	375
	ν_{36}	CH ₂ antisym. stretch	2975	2972	...	2911
	ν_{37}	CH ₂ twist	1068	1079	1035	1038
	ν_{38}	CH out-of-plane wag	928	936	567	568
	ν_{39}	CH ₂ rock ^d	781	785	493	483
	ν_{40}	CH out-of-plane wag ^d	715	720	737	747
	ν_{41}	Benzene ring bend	386	397	245	250
	ν_{42}	Ring flap	209	213	105	109

^aReference 8.^bThe experimental frequencies given for vibrations of A₂, B₁, and B₂ symmetry in the S₁(π, π^*) electronic excited state were determined from overtone or combination bands.^cCASSCF(6,6)/aug-cc-pVTZ calculations. Scaling factor: 0.905.^dRepresent pairs of coupled vibrations.

S₀ ground state but still has two very low-frequency out-of-plane ring modes, ν_{22} (A₂) skeletal twisting between the two rings at 208 cm^{-1} and ν_{42} (B₂) ring flapping at 209 cm^{-1} . The near coincidence of these frequencies was demonstrated by observation of their infrared and Raman band types.⁸ From the UV spectrum in our present study we find that the overtone levels of these vibrations are in Fermi resonance and occur at 411 and 417 cm^{-1} with mixed $2\nu_{22}$ and $2\nu_{42}$ character. Aside from the Fermi interaction, as can be seen

in Figure 6, both ν_{22} and ν_{42} , as well as two other relatively low frequency vibrations ν_{41} (B₂), the benzene ring out-of-plane bending, and ν_{21} (A₂), the benzene ring twisting, are all nearly harmonic. This is quite different from the other bicyclic molecules under discussion where the external rings display highly anharmonic character. As can be seen in Table IV, the skeletal twisting frequency for BCB is the highest at 208 cm^{-1} whereas for the other five molecules it is in the 142–178 cm^{-1} range. On the other hand, the ring-flapping

TABLE III. Fluorescence excitation and UV spectra (cm^{-1}) of BCB selected bands.

FES ^a		UV ^a		Assignment	Inferred ^b	Calculated ^c
0	vs	−276	ms	$21_1^1 42_1^1$	$-172 - 105 = -277$	
		−262	ms	$22_1^1 42_2^2$	$-54 - 204 = -258$	
		−209	ms	$22_2^0 42_0^2$	$-417 + 209 = -208$	
		−183	ms	$20_0^1 22_3^0$	$440 - 624 = -184$	
		−172	ms	21_1^1	$314 - 486 = -172$	
		−154	s	$22_1^1 42_1^1$	$-54 - 105 = -159$	
		−144	s	41_1^1	$245 - 386 = -141$	
		−114	ms	22_2^2	$301 - 417 = -116$	
		−105	s	42_1^1	$105 - 209 = -104$	
		−86	m	$40_1^1 42_1^1$	$20 - 105 = -85$	
		−76	s	14_1^1	$464 - 539 = -75$	
		−71	mw	34_1^1	$564 - 634 = -70$	
		−54	mw	22_1^1	$153 - 208 = -55$	
		−48	mw	$20_0^1 21_1^0$	$440 - 486 = -46$	
		−38	s	35_1^1	$366 - 404 = -38$	
		−28	mw	$35_1^1 42_2^4$	$-38 + 8 = -30$	
		−18	mw	$18_0^1 20_1^0$	$656 - 670 = -14$	
		0	vs	0_0^0		
		8	mw	42_2^4	$420 - 411 = 9$	
		20	w	40_1^1	$737 - 715 = 22$	
		63	mw	$19_0^1 21_1^0$	$549 - 486 = 63$	
		105	ms	42_1^3	$209 - 105 = 104$	
				$21_0^1 22_1^0$	$314 - 208 = 106$	
209	ms	209	ms	42_0^2		$2 \times 109 = 218$
301	w	301	w	22_0^2		$2 \times 157 = 314$
420	vw	420	mw	42_0^4	$2 \times 209 = 418$	
463	mw	464	vw	14_0^1		465
466	mw	467	m	$21_0^1 22_0^1$	$314 + 153 = 467$	
485	m	484	mw	41_0^2		$2 \times 250 = 500$
626	vw	626	mw	21_0^2		$2 \times 312 = 624$
733	ms	731	mw	35_0^2		$2 \times 375 = 750$
				$27_0^1 34_1^0$	$1364 - 634 = 730$	
740	s	740	s	13_0^1		713
875	m	875	mw	20_0^2		$2 \times 450 = 900$
893	ms	892	w	11_0^1		843
900	s	900	s	12_0^1		868
940	mw	940	vw	$35_0^2 42_0^2$	$731 + 209 = 940$	
949	w	949	w	$14_0^1 41_0^2$	$464 + 485 = 949$	
				$13_0^1 42_0^2$	$740 + 209 = 949$	
977	vw	978	w	$40_0^1 41_0^1$	$737 + 245 = 982$	
986	vvw	987	w	39_0^2		2×483
1094	m	1094	ms	19_0^2		$2 \times 502 = 1004$
1113	mw	1113	m	10_0^1		1112
1130	m	1129	w	34_0^2		$2 \times 567 = 1134$
1133	ms	1133	m	38_0^2		$2 \times 568 = 1136$
1169	w	1167	m	8_0^1		1170
1208	s	1208	s	9_0^1		1209
		1246	vw	21_0^4	$2 \times 626 = 1252$	
1313	mw	1313	w	18_0^2		$2 \times 635 = 1270$
1343	mw	1342	vw	$38_0^2 42_0^2$	$1133 + 209 = 1342$	
		1363	mw	$12_0^1 14_0^1$	$900 + 464 = 1364$	

TABLE III. (*Continued.*)

FES ^a		UV ^a		Assignment	Inferred ^b	Calculated ^c
1370	m	1370	mw	7_0^1		1360
1404	mw	1402	w	6_0^1		1454
1457	w	1458	vw	35_0^4	$2 \times 731 = 1462$	
1470	w	1471	w	40_0^2		$2 \times 747 = 1494$
				$13_0^1 35_0^2$	$740 + 731 = 1471$	
1477	s	1477	ms	13_0^2	$2 \times 740 = 1480$	
1493	mw	1491	w	5_0^1		1484
1517	m	1517	w	$11_0^1 21_0^2$	$892 + 626 = 1518$	
1593	vw	1594	vvw	$14_0^1 34_0^2$	$464 + 1129 = 1593$	
1597	w	1599	vvw	$14_0^1 38_0^2$	$464 + 1133 = 1597$	
1623	mw	1623	mw	$11_0^1 35_0^2$	$892 + 731 = 1623$	
		1629	vw	$11_0^1 13_0^1$	$892 + 740 = 1632$	
				$8_0^1 14_0^1$	$1167 + 464 = 1631$	
1633	w	1633	w	33_0^2		$2 \times 825 = 1650$
1640	w	1639	vw	$12_0^1 13_0^1$	$900 + 740 = 1640$	
1644	s	1643	s	4_0^1		1679
1646	w	1646	mw	$32_0^1 34_0^1$	$1085 + 564 = 1649$	
		1765	w	$11_0^1 20_0^2$	$892 + 875 = 1767$	
		1785	w	11_0^2	$2 \times 892 = 1784$	
		1793	m	$11_0^1 12_0^1$	$892 + 900 = 1792$	
		1810	mw	$10_0^1 42_2^0$	$2222 - 411 = 1811$	
		1833	mw	$7_0^1 14_0^1$	$1370 + 464 = 1834$	
				$13_0^1 19_0^2$	$740 + 1094 = 1834$	
		1871	m	$13_0^1 38_0^2$	$740 + 1133 = 1873$	
		1904	w	$32_0^1 33_0^1$	$1085 + 819 = 1904$	
		1910	vw	$8_0^1 13_0^1$	$1167 + 740 = 1907$	
		1931	w	17_0^2		$2 \times 962 = 1924$
		1943	m	31_0^2		$2 \times 972 = 1944$
		1946	m	$9_0^1 13_0^1$	$1208 + 740 = 1948$	
		1957	vvw	$5_0^1 14_0^1$	$1491 + 464 = 1955$	
		2003	w	$10_0^1 11_0^1$	$1113 + 892 = 2005$	
		2015	vw	$10_0^1 12_0^1$	$1113 + 900 = 2013$	
		2031	mw	$35_0^1 37_0^2$	$-38 + 2069 = 2031$	
		2041	m	$10_0^1 14_0^2$	$1113 + 927 = 2040$	
		2053	vw	$31_0^1 32_0^1$	$972 + 1085 = 2057$	
				$13_0^1 18_0^2$	$740 + 1313 = 2053$	
		2069	vw	37_0^2		$2 \times 1038 = 2076$
		2092	vvw	$4_0^1 14_0^1$	$1633 + 464 = 2097$	
		2105	mw	$7_0^1 13_0^1$	$1370 + 740 = 2110$	
		2116	m	$10_0^2 42_1^1$	$2222 - 105 = 2117$	
		2153	vvw	$8_0^1 39_0^2$	$1167 + 987 = 2154$	
		2222	vw	10_0^2	$2 \times 1113 = 2226$	
				$5_0^1 35_0^2$	$1491 + 731 = 2222$	
		2239	w	$14_0^2 18_0^2$	$927 + 1313 = 2240$	
				$10_0^1 34_0^2$	$1113 + 1129 = 2242$	
		2256	vw	34_0^4	$2 \times 1129 = 2258$	
		2300	vvw	16_0^2		$2 \times 1169 = 2338$
		2376	vw	30_0^2		$2 \times 1174 = 2378$
		2384	w	$4_0^1 13_0^1$	$1643 + 740 = 2383$	
		2411	vvw	$14_0^1 31_0^2$	$464 + 1943 = 2407$	
		2521	vvw	29_0^2		$2 \times 1261 = 2522$

TABLE IV. Skeletal vibrational frequencies (cm^{-1}) of BCB and related molecules in the ground (S_0) and excited (S_1) state.

		S_0						$S_1(\pi, \pi^*)$					
		BCB	IND	TET	14BZD	13BZD	14DHN	BCB	IND	TET	14BZD	13BZD	14DHN
A ₁	Benzene C–C stretch	1605	1589	1581	1599	1587	1571	1646	(1627)	(1640)	(1502)	(1608)	(1625)
	Benzene C–C stretch	1466	1474	1496	1500	1503	1497	1491	(1493)	(1531)	(1498)	(1559)	(1518)
	Benzene C–C stretch	1344	1318	1295	1307	1309	1288	1370	(1409)	(1435)	(1391)	(1381)	1337
	Benzene C–C stretch	1001	1025	1035	1028	1035	1041	892	(934)	971	994	(1051)	951
	Benzene angle bend	539	610	578	566	588	586	464	460	480	531	525	459
A ₂	Benzene ring twist	670	(714) ^a	700	717	712	703	440	485	521	(502)	682	(447)
	Benzene ring twist	486	499	501	553	536	510	314	345	330	363	374	(360)
	Skeletal twist	208	178	142	166	158	148	153	137	94	140	102	92
B ₁	Benzene C–C stretch	1596	1610	1598	1602	1614	1603	1500	(1446)	(1449)	(1566)	(1665)	(1415)
	Benzene C–C stretch	1458	1460	1437	1462	1460	1460	1364	(1394)	(1406)	(1437)	(1481)	(1406)
	Benzene ring bend	855	832	804	834	853	885	819	(821)	(764)	888	(750)	867
	Benzene ring bend	634	579	586	643	698	765	564	535	545	(530)	(574)	(707)
B ₂	Benzene ring bend	386	412	436	(466)	430	427	245	273	270	(370)	255	298
	Ring flap	209	248	257	297	274	231	105	176	(140)	(119)	194	115
	Reference	8	1	2	3–5	6	7	This work	1	2	3–5	6	7

^aFrequencies in parentheses are calculated values.

VI. CONCLUSIONS

Ab initio computations have been carried out to calculate the structure of benzocyclobutane in its $S_1(\pi, \pi^*)$ excited state and to compare it with the S_0 ground state. The results were compared to similar computational results for the ground and excited states of five related molecules. The *ab initio* calculations were also helpful in assigning the fluorescence excitation and ultraviolet absorption spectra. The majority of the vibrational frequencies, including all of the low-frequency modes, were assigned for the excited state and compared to the ground state data. Of special interest were the large frequency decreases of the out-of-plane skeletal and benzene ring modes in the excited state reflecting the decreased molecular rigidity resulting from a decrease in the π bonding.

ACKNOWLEDGMENTS

J.L. wishes to thank the Robert A. Welch Foundation (Grant No. A-0396) for financial support. S.K. received funding from the Intramural Research Program of the National Institutes of Health (NIH), National Library of Medicine (NLM). Computations by J.L. and E.J.O. were carried out on the Texas A&M University Department of Chemistry Medusa computer system funded by the National Science Foundation, Grant No. CHE-0541587 and S.K. utilized the Biowulf Linux cluster at the NIH, Bethesda, MD (<http://biowulf.nih.gov>). The Laboratory for Molecular Simulation provided the Semichem AMPAC/AGUI software used by J.L. and E.J.O.

¹A. Arp, N. Meinander, J. Choo, and J. Laane, *J. Chem. Phys.* **116**, 6648 (2002).

²J. Yang, M. Wagner, and J. Laane, *J. Phys. Chem. A* **111**, 8429 (2007).

³J. Yang, J. Choo, O. Kwon, and J. Laane, *Spectrochim. Acta A* **68**, 1170 (2007).

⁴J. Yang, M. Wagner, and J. Laane, *J. Phys. Chem. A* **110**, 9805 (2006).

⁵D. Autrey, J. Yang, and J. Laane, *J. Mol. Struct.* **661–662**, 23 (2003).

⁶K. McCann, M. Wagner, A. Guerra, P. Coronado, J. R. Villareal, J. Choo, S. Kim, and J. Laane, *J. Chem. Phys.* **131**, 044302-1–044302-9 (2009).

⁷M. Rishard, M. Wagner, J. Choo, and J. Laane, *J. Phys. Chem. A* **113**, 7753 (2009).

⁸E. J. Ocola, H. W. Shin, and J. Laane, "Infrared and Raman spectra and theoretical calculations for benzocyclobutane in its electronic ground state," *Spectrochim. Acta* (to be published).

⁹K. Morris, Ph.D. thesis, Texas A&M University, 1998.

¹⁰Z. Arp, Ph.D. thesis, Texas A&M University, 2001.

¹¹J. Laane, *J. Phys. Chem. A* **104**, 7715 (2000).

¹²S. Sakurai, N. Meinander, K. Morris, and J. Laane, *J. Am. Chem. Soc.* **121**, 5056 (1999).

¹³W.-Y. Chiang, and J. Laane, *J. Chem. Phys.* **100**, 8755 (1994) and references therein.

¹⁴C. M. Cheatham, M.-H. Huang, and J. Laane, *J. Mol. Struct.* **377**, 93 (1996).

¹⁵C. M. Cheatham, M.-H. Huang, N. Meinander, M. B. Kelly, K. Haller, W.-Y. Chiang, and J. Laane, *J. Mol. Struct.* **377**, 81 (1996).

¹⁶J. Laane, J. Zhang, W.-Y. Chiang, P. Sagear, and C. M. Cheatham, "Jet-cooled fluorescence excitation spectra and carbonyl wagging potential energy functions of cyclic ketones in their electronic excited states," in *Topics in Molecular Organization and Engineering, Vol. 12: Structure and Dynamics of Non-Rigid Molecular Systems*, edited by Y. G. Smeyers (Kluwer Academic Publishers, Dordrecht, Netherlands, 1995), pp. 181–201.

¹⁷M. W. Schmidt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, *J. Comput. Chem.* **14**, 1347 (1993).

¹⁸M. S. Gordon and M. W. Schmidt, "Advances in electronic structure theory: GAMESS a decade later," in *Theory and Applications of Computational Chemistry: The First Forty Years*, edited by C. E. Dykstra, G. Frenking, K. S. Kim, and G. E. Scuseria (Elsevier Publishing, Amsterdam, Netherlands, 2005), Chap. 41, pp. 1167–1189.

¹⁹P. Boopalachandran, S. Kim, J. Choo, and J. Laane, *Chem. Phys. Lett.* **514**, 214 (2011).

²⁰B. M. Bode and M. S. Gordon, *J. Mol. Graphics Mod.* **16**, 133 (1998).

²¹M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford, CT, 2009.

²²D. Autrey, J. Choo, and J. Laane, *J. Phys. Chem. A* **105**, 10230 (2001).

- ²³E. J. Ocola, L. E. Bauman, and J. Laane, *J. Phys. Chem. A* **115**, 6531 (2011).
- ²⁴E. J. Ocola, A. A. Al-Saadi, C. Mlynek, H. Henning, and J. Laane, *J. Phys. Chem. A* **114**, 7457 (2010).
- ²⁵E. J. Ocola, T. Brito, K. McCann, and J. Laane, *J. Mol. Struct.* **978**, 74 (2010).
- ²⁶D. Autrey, Z. Arp, J. Choo, and J. Laane, *J. Chem. Phys.* **119**, 2557 (2003).
- ²⁷See <http://www.semichem.com> for the information about AGUI program from Semichem, Inc., Shawnee, KS 66216.
- ²⁸See supplementary material at <http://dx.doi.org/10.1063/1.4858412> for fluorescence excitation and UV transition frequencies (cm^{-1}) of BCB.