as well as in solution. Despite the large difference in solvent effect, both the diazoalkane and nitrile oxide are effective reagents for 1,3-dipolar addition.[34] Hence, it would be reasonable to conclude that the charge effect of these species is not important in 1,3-dipolar cycloaddition.

Conclusions

In this paper, we have reported a correlated version of Onsager's formalism of a reaction field method for studying solvent effects. We have applied this model to study solvent effects on conformational equilibria, rotational barriers, and charge distributions and molecular properties of ionic and neutral dipolar species. This method is able to provide reasonable estimates of the solvent effects in conformational equilibria and rotational barriers. Furthermore, it provides a good qualitative understanding of the effect of electrostatic interaction of the ionic or neutral dipolar species with its surrounding medium. Thus, Onsager's reaction field theory appears to be a promising approach to examine the nonspecific electrostatic solvent–solute interaction. We are currently applying this model to study solvent effects on reaction rates and excited states.[24] The use of more realistic cavity shapes also is being studied.

Calculations

The calculations were carried out with the GAUSSIAN-91 system of programs[20] and were run on a Multiflow Trace 14/200 computer. Standard basis sets were used.[22] The analysis of the wave functions was carried out with the PROAIM programs[35] running on a DEC-3100 workstation.

Acknowledgment. The investigation was supported by a grant from the National Institutes of Health and by Lorentzian Inc.

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(35) Biegler-Konig, F. W.; Bader, R. F. W.; Tang, T.-H. *J. Comput. Chem.* **1982**, *3*, 317.

Assignment of the $\tilde{A}$ State in Bicyclobutane. The Multiphoton Ionization Spectrum and Calculations of Transition Energies

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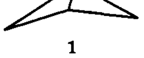
Contribution from the Departments of Chemistry, Yale University, New Haven, Conneticut 06511, State University of New York, Stony Brook, New York 11794, and Carnegie Mellon University, Pittsburgh, Pennsylvania 15213. *Received October 29, 1990*

Abstract: The two-photon spectrum of bicyclo[1.1.0]butane has been obtained via resonance enhanced multiphoton ionization. A comparison with the one-photon spectrum shows that the first band at 44000–48000 cm^{-1} is an allowed A_1 transition corresponding to an s Rydberg state. Vibrational cooling in a jet expansion causes some of the lower energy components of the spectrum to disappear, indicating that they are hot bands. The 0–0 band origin of the transition was found to be 45 944 cm^{-1}. The vibrational components for the parent and for the *1,3-d_2* and *2,2,4,4,-d_4* isotopomers have been assigned. The transition energies have been calculated at the CIS/6-311(2+)G* level of theory, and an A_1 state is predicted to have the lower energy. The structure of the excited state was calculated and found to be essentially the same as that of the bicyclobutane radical cation. The vibrational frequencies also were calculated and agreed well with the observed frequencies. The nature of the lower energy transitions is discussed with the aid of charge density difference maps for going from the ground state to each of the first 20 excited states. All of these may be regarded as Rydberg states.

Introduction

Bicyclobutane (**1**) is an ideal model system for the study of the electronic structure of saturated small-ring molecules because it is of a size that is both experimentally interesting and theoretically tractable. This strained hydrocarbon consists of two cyclopropane rings joined by a common C–C bond. The microwave spectrum[1] showed the molecule to have C_{2v} symmetry in the ground electronic state with an angle between the two rings of 122.7°. Further information on the ground state was obtained from a recent reassignment of the ground-state vibrations coupled with a normal coordinate analysis.[2]



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Information on the structure of bicyclobutane in excited electronic states was provided by the ultraviolet absorption spectrum that was obtained and analyzed in one of our laboratories.[3,4] The UV spectra of bicyclobutane-d_0, -d_2, and -d_4 are reproduced in Figures 1–3. The spectrum for each molecule exhibits three regions of well-resolved vibrational structure, two of which exhibit almost identical vibrational features and appear to be related in some way. The region of most pronounced structure for each molecule is found in the lowest energy band ($\tilde{A}$) which is observed between 44000 and 48000 cm^{-1} and shown in expanded form at the top of each figure. A second structured region, which exhibits similar vibrational spacing to the first region, appears between 58000 and 62000 cm^{-1}. For both of these regions, the vibrational spacing shows the expected variation with deuteration. An additional region of structure appears between 48000 and 51000 cm^{-1}. In bicyclobutane, the vibrational spacing in this third region is approximately twice that in the other two regions.

Bicyclobutane has C_{2v} symmetry, and therefore a one-photon transition to an A_1, B_1, or B_2 electronic state is electric dipole allowed, whereas a transition to an A_2 state is forbidden. On the

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(1) Cox, K. W.; Harmony, M. D.; Nelson, G.; Wiberg, K. B. *J. Chem. Phys.* **1969**, *50*, 1976.

(2) Wiberg, K. B.; Waddell, S. T.; Rosenberg, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 2184.

(3) Wiberg, K. B.; Ellison, G. B.; Peters, K. S. *J. Am. Chem. Soc.* **1977**, *99*, 3941.

(4) Wiberg, K. B.; Peters, K. S.; Ellison, G. B.; Alberti, F. *J. Am. Chem. Soc.* **1977**, *99*, 3946.

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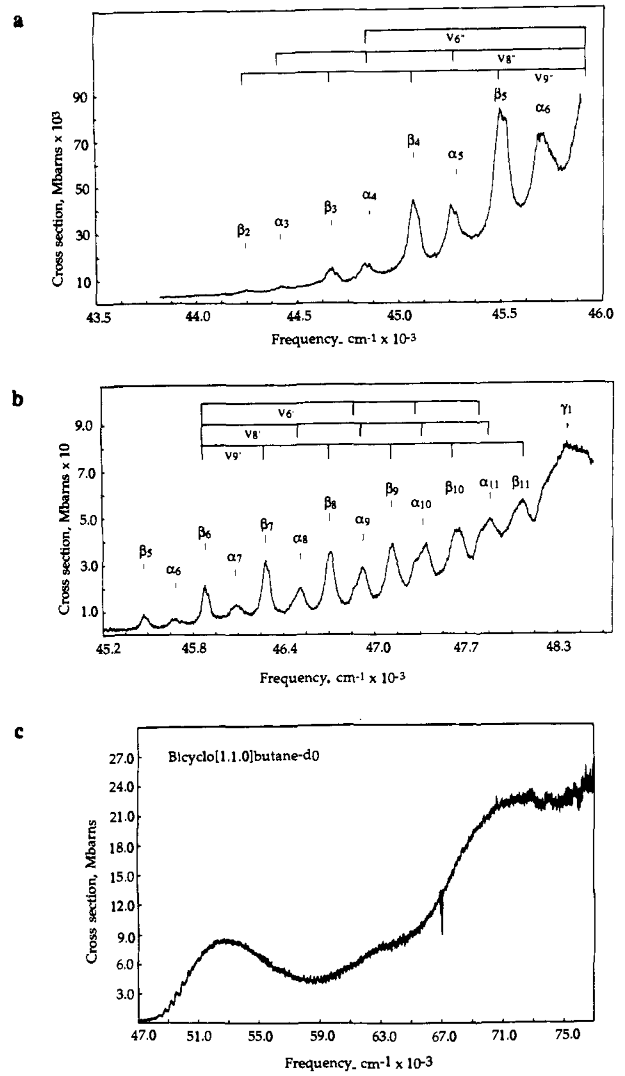

Figure 1. The ultraviolet absorption spectrum of gas-phase bicyclobutane (bottom). Due to its low relative intensity, the absorption region corresponding to the A state is plotted separately (upper spectra). The resolution is approximately 25 cm^{-1}.

basis of the relative weakness of the low-energy (Ã) transition, it was assigned as a vibronically induced transition to an A_2 state.[3] A vibrational contour analysis suggested that the inducing vibrational modes were of b_1 symmetry.[4]

These early experimental results were not in accord with the then available molecular orbital calculations which predicted a lowest energy valence state of B_1 symmetry.[5] This state was calculated to result from promotion of an electron from the highest occupied MO of a_1 symmetry (involving bonding along the central C–C bond) to an antibonding orbital of b_1 symmetry. Since a transition to a B_1 state is electronically allowed, the absorption band should be strong and the intense band at 53 000 cm^{-1} has been assigned to this transition.

In this work, we have reinvestigated both the theory and the spectroscopy of the Ã state to definitively determine the nature and assignment of this state. The two-photon resonance ionization spectrum is found to exhibit the same spectral features observed in the one-photon UV spectrum, strongly suggesting that the electronic state is allowed in both one- and two-photons, i.e. not of A_2 symmetry. We have also carried out additional theoretical calculations which show that more flexible basis sets lead to a lowest unoccupied molecular orbital having a_1 symmetry and that CIS calculations find the first excited state to have A_1 symmetry. Our results are in accord with an assignment of the Ã state to an s Rydberg state. In light of the new electronic state assignment, a reanalysis of the observed vibrational bands in the Ã state also is presented.

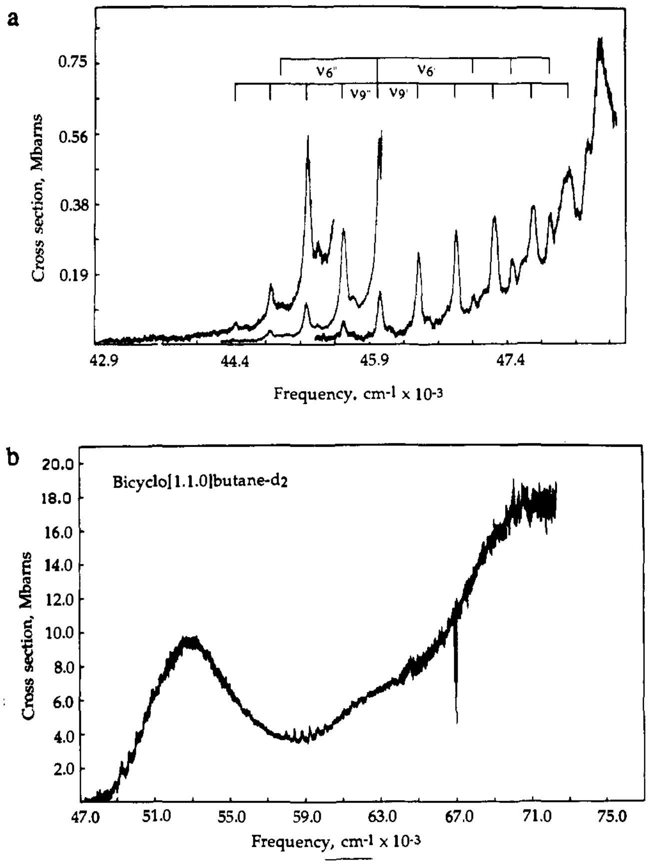

Figure 2. The ultraviolet absorption spectrum of bicyclobutane-*1,3*-d_2.

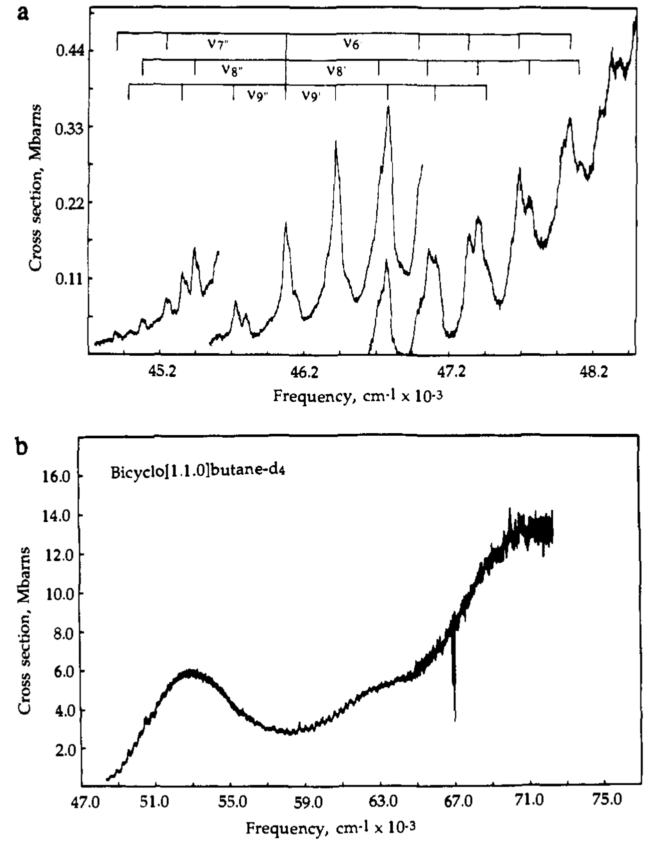

Figure 3. The ultraviolet absorption spectrum of bicyclobutane-*2,2,4,4*-d_4.

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(5) (a) Jorgensen, W. L.; Salem, L. *The Organic Chemist's Book of Orbitals*; Academic Press: New York, 1973; pp 203–205. (b) Reference 3.

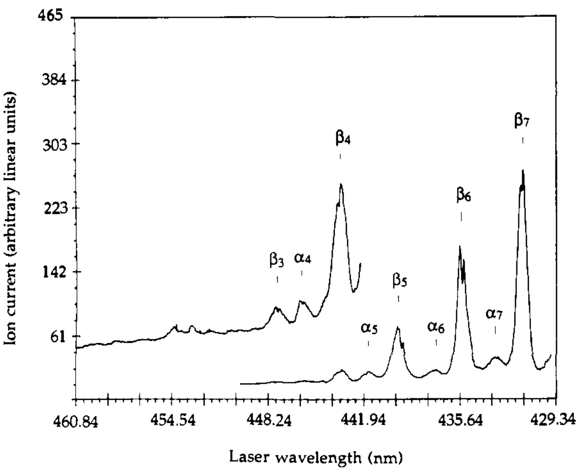

Figure 4. The 2 + 2 resonance enhanced multiphoton ionization spectrum of bicyclobutane in the gas phase at room temperature. The lower energy region of the A state is shown. The MPI signal has been normalized to the square of the laser power.

Experimental Section

Two-photon absorption spectra of gas-phase bicyclobutane were obtained in a static room temperature MPI cell and in a molecular beam. For the cell experiments, radiation from a XeCl excimer pumped dye laser was directed into the cell and focused by a 4-in. lens mounted inside the cell. The laser energy was typically less than 0.8 mJ, although for the very weak region between 43000 and 45200 cm^{-1} a laser energy of 1.5 mJ was used. The vapor pressure of bicyclobutane inside the cell was 5.0 Torr. Ionization occurred within a stainless steel cylinder, mounted inside the cell, to which a negative voltage of 300–450 V had been applied. Ejected electrons were collected on a thin wire inside the cylinder and the current amplified before passing to the digitizer for data collection. Gated regions of the signal were monitored as a function of wavelength.

Multiphoton ionization experiments also were carried out in a molecular beam to vibrationally cool bicyclobutane prior to ionization and detection. Helium at a pressure of 40 psi was passed over bicyclobutane in a sample chamber at −30 °C and expanded out of a pulsed nozzle. The beam was skimmed once in a differentially pumped vacuum chamber and then ionized. The ions were repelled 90° out of the molecular beam path into a time-of-flight mass spectrometer. No parent mass peak was observed and spectra were obtained monitoring the fragment ions (C_2H_x and C_3H_x). The ion signal was preamplified before digitizing.

The resolution of all the two photon spectra (static and beam) was 2 cm^{-1}. Higher resolution was deemed unnecessary by the large fwhm (about 75 cm^{-1}) of the vibrational bands.

Results and Discussion

I. Symmetry of the Ã State. a. Selection Rules. For a molecule of C_{2v} symmetry, a one-photon transition from a ground electronic state of A_1 symmetry to an excited electronic state of A_1, B_1, and B_2 is electric dipole allowed. Vibrational structure for these states must involve totally symmetric (a_1) vibrational modes. A one-photon electronic transition to an A_2 state is electric dipole forbidden. However, vibrations of a_2, b_1, and b_2 symmetry can cause a transition to an A_2 state of bicyclobutane to be vibronically allowed.

As has been well documented, transitions involving two photons are governed by different selection rules than those for one-photon transitions.[6] A two-photon transition from an A_1 ground state to an electronic state of any symmetry—A_1, A_2, B_1, and B_2—is electric dipole allowed. As in the one-photon case, the allowed vibrations active in a two-photon transition are of a_1 symmetry.

b. Two-Photon Absorption Spectrum. The two-photon absorption spectrum of bicyclobutane as detected by multiphoton ionization is shown in Figures 4 and 5. The vibrational bands seen in this spectrum duplicate the transition energies observed in the one-photon spectrum. (There are some differences in the relative intensities, however, which is not unusual since different factors determine the intensity in the two types of spectra.) It seems clear that the vibrations active in the one-photon spectrum are also active in the two-photon spectrum. For this reason, we have adopted the same band labels used in the analysis of the one-photon spectrum.

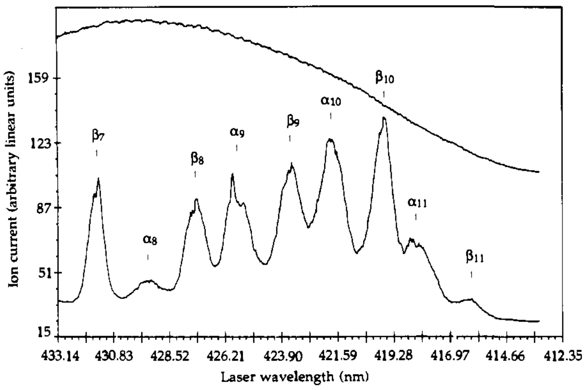

Figure 5. The MPI spectrum of the higher energy region of the A state of bicyclobutane. The gas-phase spectrum was obtained at room temperature. The dye curve is shown. This spectrum has not been normalized to the laser power.

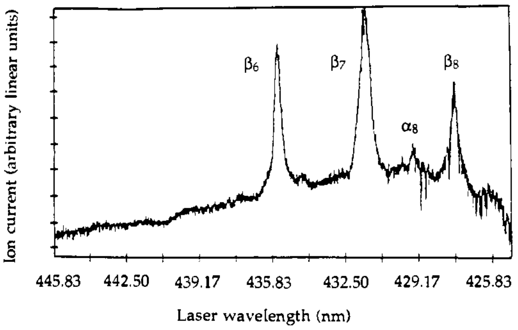

Figure 6. The MPI spectrum of bicyclobutane in a molecular beam. Note that β_5 does not appear in this vibrationally cooled spectrum even though its absorption energy (439 nm) is near the maximum of the dye curve. The small peak just to the blue of β_6 is probably an impurity since it was not always observed in spectra of this region. The sharp negative peaks in the higher energy region are due to spurious noise. This spectrum has not been normalized to the laser power.

To carry out an analysis of the vibrational components of the A state, it is first necessary to determine the location of the 0–0 band origin. Determination of the origin is often difficult due to the presence of hot bands, which result from absorption from excited vibrational levels populated at higher temperatures. The vibrational cooling realized by expansion of the molecule in a molecular beam can be effective in reducing the intensity of the hot bands, and even eliminating them from the spectrum. The two-photon absorption spectrum of bicyclobutane in a molecular beam is shown in Figure 6. It can be seen in this spectrum that all bands at lower energy than β_6 are no longer observed. Most striking is the absence of β_5 which showed considerable intensity in the room temperature spectrum. (It should appear around 439 nm.) Clearly, β_5 can be assigned as a hot band. Assuming complete vibrational cooling (and that the origin has observable intensity)[7] one can assign the origin band to the lowest energy band still seen in Figure 6, β_6, which appears at 45944 cm^{-1} in the UV spectrum. To substantiate this assignment, we note that the differences in energy between a hot band and the origin correspond exactly to the ground-state vibrational frequencies, which are very well known for bicyclobutane.[2] The energy difference between β_6 and β_5 is 425 cm^{-1}, which corresponds to the vibrational frequency of the a_1 vibration, v_9, appearing in the

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(6) Johnson, P. M. *Acc. Chem. Res.* **1980**, *13*, 20.

(7) If the A state had A_2 symmetry, the origin would *not* be expected to have observable intensity. Following through with our assumption of observable intensity leads to a remarkably self-consistent assignment of the spectra of all three isotopomers which is in complete agreement with the results of our calculations.

ground state at 422.5 cm^{-1}, as mentioned previously. Population in the $v = 1$ level of the ground state would be appreciable and is in accord with the relatively strong intensity for β_5 in the room temperature spectrum. The energy difference between another hot band, α_5, and β_6 is 663 cm^{-1}, which agrees well with the frequency of the ground-state v_8 mode at 656.9 cm^{-1}. This mode is also of a_1 symmetry. Using β_6 as the origin, we can readily assign all the hot bands in bicyclobutane. By assuming appropriate blue shifts of the origins of the deuterated derivatives, we find that the hot bands in these spectra can be assigned to the same a_1 vibrations taking into account the known shifts in the ground-state vibrational frequencies. Hence we assign the β_6 band of bicyclobutane as the band origin. Since the spectrum exhibits only a_1 vibrational components, we can eliminate the possiblity of an A_2 excited electronic state.

II. Rydberg Character of the Ã State. The observed spectral features strongly indicate that the Ã state is Rydberg, and not valence, in character. It has previously been assumed that resolved vibrational features attributable to Rydberg states would not be observed in ultraviolet spectra of saturated hydrocarbons. This is due to the fact that the highest occupied MO of such molecules usually involves C–H bonding and the excited-state potential wells tend to be shallow and shifted with respect to the ground state. Absorption from the ground state excites continuum regions of these states—and broad, diffuse spectra result.[8] As convincingly shown by Robin in the case of cyclopropane[9] this assumption is not necessarily valid when the highest occupied MO does not involve C–H bonding. In the UV spectrum of this saturated cyclic hydrocarbon, two regions of vibrational structure are observed. The HOMO of cyclopropane involves delocalized C–C bonding, and he assigns the two structured regions to the 3p and 4p Rydberg states. Our calculations (see below) indicate that the HOMO of bicyclobutane is bonding along the central C–C bond (i.e. does not involve much C–H bonding), and it seems possible, therefore, that Rydberg states may be observed.

The well-known equation for determining the energies of the Rydberg state is

$$E = \mathrm{IP} - R/(n - \delta)^2$$

where R is the Rydberg constant (109737 cm^{-1}), IP is the ionization potential (8.700 eV (adiabatic) for bicyclobutane),[10] n is the principal quantum number, and δ is the quantum defect which has characteristic values for s, p, d, and f Rydberg orbitals. Of interest here is the fact that s orbitals for hydrocarbons typically have quantum defects of 0.9–1.1. Substituting in the value for the Ã state origin as E_n, a principal quantum number of 3 yields a quantum defect of 0.9. Hence, these results suggest that the Ã state is a 3s Rydberg state. This conclusion also has been reached by Robin.[11]

As will be seen in the later section describing the new theoretical calculations, a state of A_1 symmetry is now predicted as the lowest energy excited state. An assignment of this state to a 3s Rydberg state is in complete accord with the results of these calculations. As s orbital transforms under the totally symmetric representation of the C_{2v} symmetry group, hence has a_1 symmetry.

According to our assignment, the Ã state of bicyclobutane results from promotion of an electron from a bonding C–C orbital to a Rydberg orbital. The expected geometry change in this state is a lengthening of the central C–C bond. The vibrations active in the transition should involve stretching of this bond. The ν_9 and ν_8 vibrations, which have already been identified in the spectrum, involve a large component of this motion as indicated in the ground-state normal-coordinate analysis. In fact, all of the assigned vibrational modes in the spectra of bicyclobutane include a contribution from this stretch.

Table I. Bicyclobutane Vibrational Frequencies (cm^{-1}) of the Ground Electronic State

a_1 modes	d_0	d_2	d_4
ν_1	3131.3	2354.8	3131.3
ν_2	3043.7	3044.6	2293.5
ν_3	2935.0	2935.0	2157.5
ν_4	1501.3	1490.4	1310.4
ν_5	1266.0	1226.8	1059.0
ν_6	1080.7	1083.1	923.9
ν_7	838.8	827.8	824.4
ν_8	656.9	510.2	627.5
ν_9	422.5	403.1	354.4

Table II. Transition Frequencies (cm^{-1}) and Assignments for Bicyclobutane-d_0

band	one-photon UV[a]	two-photon MPI[b]	$\Delta\nu$[c]	assignment
		a. α Bands		
α_1	43674*	43642	−2270	$8_1^0 9_4^0$
α_2	43995*	44009	−1949	$8_1^0 9_3^0$
α_3	44437		−1507	$8_1^0 9_2^0$
α_4	44861	44838	−1083	$8_1^0 9_1^0$, 6_1^0
α_5	45281	45280	−663	8_1^0, $6_1^0 9_0^1$
α_6	45707	45720	−237	$8_1^0 9_0^1$, $8_0^1 9_0^2$, $6_1^0 9_0^2$
α_7	46132	46159	188	$8_1^0 9_0^2$, $8_0^1 9_1^0$, $6_1^0 9_0^3$, $6_0^1 9_2^0$
α_8	46566*	46577	622	8_0^1, $6_0^1 9_0^4$, $6_0^1 9_1^0$
	46938[d]		994	6_0^1
α_9	46989	46963, 47014	1045	$8_0^1 9_0^1$
	47339[d]		1395	$6_0^1 9_0^1$
α_{10}	47405*	47409	1461	$8_0^1 9_0^2$
	47807[d]		1863	$6_0^1 9_0^2$
α_{11}	47865*	47797	1921	$8_0^1 9_0^3$
		b. β Bands		
β_1	43861*		−2083	9_5^0
β_2	44259	44238	−1685	9_4^0
β_3	44681	44682	−1263	9_3^0
β_4	45104	45096	−840	9_2^0
β_5	45519	45475, 45515	−425	9_1^0
β_6	45944	45910, 45932	0	0–0 origin
β_7	46363	46334, 46352	419	9_0^1
β_8	46787	46796	843	9_0^2
β_9	47192*	47228	1248	9_0^3
β_{10}	47617*	47651	1693	9_0^4
β_{11}	48086*	48069	2142	9_0^5

[a] The spectral resolution used in obtaining the unstarred frequencies in the one-photon spectrum was 0.3 cm^{-1}. The spectral resolution used in obtaining the starred frequencies was 25 cm^{-1}. [b] The spectral resolution used in obtaining the two-photon spectra was 2 cm^{-1}. Due to the width of the bands, however, the error in the band positions was on the order of ±5 cm^{-1} for the more intense bands and ±15 cm^{-1} for the weak bands. [c] This represents the difference in frequency from the origin and is calculated by using the one-photon UV transition frequencies. [d] These transitions frequencies are estimated from a plot of the UV spectrum.

III. Vibrational Assignments. As has already been demonstrated, hot bands can be very helpful in making assignments of excited-state vibrational bands. Since they represent absorption from excited vibrational levels of the ground electronic state, the difference in energy between the origin and a hot band is exactly equal to a ground-state vibrational frequency. The assigned frequencies of the a_1 vibrations for bicyclobutane-d_0, -d_2, and -d_4 are presented in Table I.[2] The assignments of the excited-state vibrational bands are given below. The assignments are remarkably consistent from molecule to molecule. Primarily, the same modes are found in all three spectra, as evidenced by hot bands with deuterium shifts which exactly match the ground-state shifts. Moreover, the vibrational motions associated with the modes all involve some component of the central C–C stretch,

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(8) Herzberg, G. *Electronic Spectra of Polyatomic Molecules*; Van Nostrand Reinhold Company: New York, 1966; p 413.

(9) Basch, H.; Robin, M. B.; Kuebler, N. A.; Baker, C.; Turner, D. W. *J. Chem. Phys.* **1969**, *51*, 52.

(10) Bombach, R.; Dannacher, J.; Stadelmann, J. P.; Neier, R. *Helv. Chim. Acta* **1983**, *60*, 701.

(11) Robin, M. *Higher Electronic States of Polyatomic Molecules*; Academic Press: New York, 1974; Vol. I, p 152.

(12) Reference 5 gives plots of the bicyclobutane MO's obtained by using small basis sets which may be compared with those obtained in this investigation. The virtual orbitals obtained in a HF calculation are those appropriate to a molecule having one additional electron. To obtain the virtual orbitals for bicyclobutane with use of good basis sets, it is necessary to carry out a calculation for the bicyclobutane radical cation.

which is to be expected since the geometry change on going to the Ã state is elongation of the C–C bond.

Bicyclobutane-d_0. The assignments and transition frequencies observed in the one-photon UV and two-photon multiphoton ionization spectra are found in Table II. We have already established that β_6 is the 0–0 origin band in bicyclobutane. Since the UV spectrum was obtained at higher resolution than the two-photon spectrum, we take the transition frequency of the β_6 band in the UV spectrum, 45944 cm^{-1}, as the most accurate value for the origin.

The β_5 band is assigned as the 9_1^0 hot band, as discussed previously. The lower β bands differ from the origin by multiples (approximately) of the 422.5-cm^{-1} frequency for the ground-state ν_9 band; hence, these can be assigned to hot bands originating from higher vibrational levels of this mode in the ground state, i.e. 9_2^0, 9_3^0, 9_4^0, and 9_5^0. The higher energy β bands (β_6 and higher) form a series with adjacent β bands spaced approximately 425 cm^{-1} apart. We assign the β bands above β_6 to excitation to successively higher vibrational levels of the Ã state ν_9 mode, i.e. 9_0^1, 9_0^2, 9_0^3, etc. The β bands, therefore, constitute a progression in ν_9 built upon the origin. The excited-state frequency for this mode does not seem to differ significantly from the ground-state value, although the actual magnitude of the change is difficult to assess due to the broad band widths (on the order of 75 cm^{-1} in the UV spectrum).

The earlier hot band analysis also indicated that the α_5 band was due to excitation from the $v = 1$ level of the ground-state ν_8 mode which has a vibrational frequency of 656.9 cm^{-1} in this state. The lower energy α bands also are assigned as hot bands. In the molecular beam spectrum, a small band appears at the energy of the α_8 band, indicating that it is not a hot band. The α_8 band has an energy that is greater than the origin by 622 cm^{-1}, and we assign the excited-state ν_8 mode to this frequency. The spacing between adjacent α bands is approximately 420 cm^{-1}, suggesting that the α bands are a progression in ν_9 built upon the ν_8 mode, i.e. the $8_1^0 9_n^m$ and $8_0^1 9_n^m$ progression.

As seen in the UV spectrum, the α_9, α_{10}, and α_{11} bands also contain a "shoulder" on the low-energy side. One also notes in the two-photon spectrum that the intensity of the α bands increases sharply at α_9. These two spectral features suggest that a second progression coincides at approximately the same energies as the $8_0^1 9_0^n$ progression. The α_4 band in the UV spectrum appears 1083 cm^{-1} below the origin. This energy difference agrees well with the ground-state frequency of the ν_6 mode, 1080.7 cm^{-1}. (Note that the α_4 band is also assigned to the $8_1^0 9_1^0$ hot band, and the total intensity is due to both bands.) The shoulder to the red of the α_9 band is 994 cm^{-1} above the origin, and this frequency is assigned to the excited-state ν_6 mode. The second progression, then, is assigned to $6_0^1 9_n^m$, a progression in ν_9 built on ν_6.

Further evidence for the validity of the above assignments is found in the spectra of the isotopomers, particularly that of bicyclobutane-d_2 where the ν_9, ν_8, and ν_6 modes are observed with the expected deuterium shifts. All of these modes involve some component of stretching along the central C–C bond (30%, 19%, and 16%, respectively), consistent with the proposed geometry difference between the ground and Ã states. Note that additional contributions to the intensities of the β bands can conceivably arise from transitions involving the ν_7 and ν_5 modes. The ground-state ν_7 mode involves 44% central C–C stretch and has a frequency of 838.8 cm^{-1}. Since the frequency is almost exactly twice that of the ν_9 mode, bands associated with these modes would be completely overlapped within the resolution of our spectra. Likewise, the ground-state ν_5 mode has a frequency of 1266 cm^{-1}, which is three times the ν_9 frequency. The vibrational motion associated with the ν_5 mode is 25% central C–C stretching.

It should be noted that we have successfully assigned all the observed bands in the bicyclobutane spectrum to a_1 vibrations. This further supports our assignment of the Ã state electronic symmetry to A_1, making the transition electronically allowed with both one and two photons.

The spectra of bicyclobutane-d_2 and -d_4 were analyzed in the same fashion, giving the assignments shown in Figures 2 and 3. A detailed analysis of these spectra is available as supplementary material.

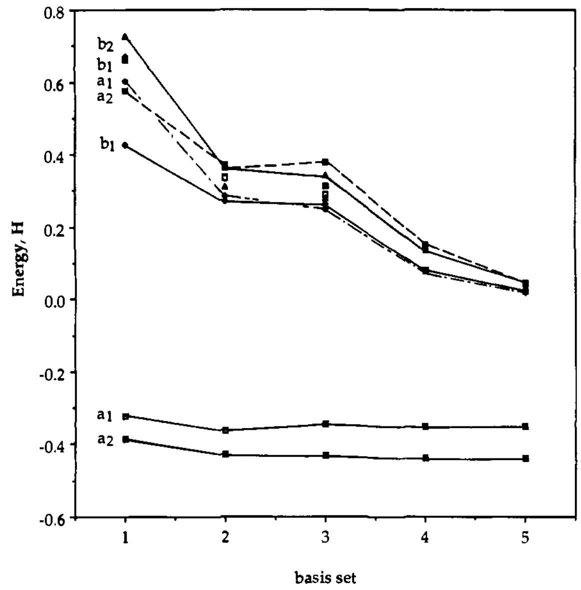


Figure 7. Molecular orbital energies for bicyclobutane. The basis sets are (1) STO-3G, (2) 3-21G, (3) 6-31G*, (4) 6-311+G*, (5) 6-311-(2+)G*.

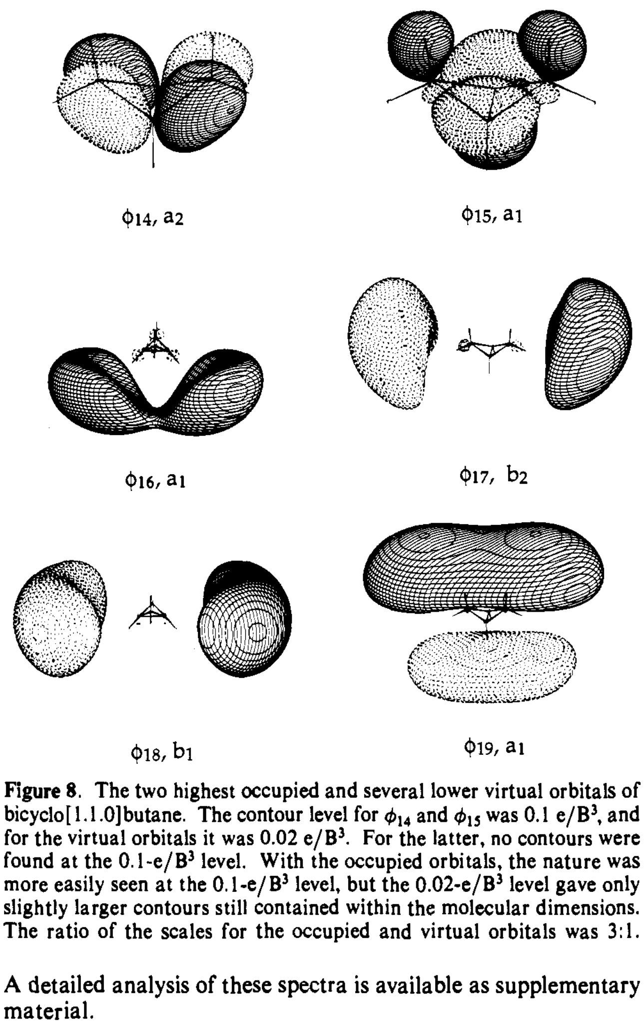
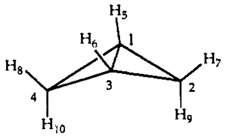


Figure 8. The two highest occupied and several lower virtual orbitals of bicyclo[1.1.0]butane. The contour level for ϕ_{14} and ϕ_{15} was 0.1 e/B^3, and for the virtual orbitals it was 0.02 e/B^3. For the latter, no contours were found at the 0.1-e/B^3 level. With the occupied orbitals, the nature was more easily seen at the 0.1-e/B^3 level, but the 0.02-e/B^3 level gave only slightly larger contours still contained within the molecular dimensions. The ratio of the scales for the occupied and virtual orbitals was 3:1.

IV. Theoretical Calculations.

Hartree–Fock calculations employing STO-3G and 3-21G basis sets have found that the highest occupied molecular orbital has a_1 symmetry and the lowest unoccupied MO has b_1 symmetry.[5] However, more flexible basis sets (6-31G* and larger) give the lowest unoccupied MO having a_1 symmetry. There is, in fact, a considerable change in ordering of the virtual MO's with increasing basis set size (Figure 7). The

Table III. Calculated Structures for Bicyclo[1.1.0]butane Ground State, $2A_1$ State, and Radical Cation



parameter[a]	ground state MP2/6-31G*	exptl	HF/6-31G*	HF/6-31+G*	$2A_1$ state CIS/6-31+G*	radical cation HF/6-31G*	MP2/6-31G*
C1–C3	1.496	1.497 ± 0.003	1.466	1.470	1.687	1.695	1.674
C1–C2	1.492	1.498 ± 0.004	1.489	1.489	1.476	1.490	1.484
C1–H5	1.080	1.071 ± 0.004	1.071	1.070	1.078	1.074	1.086
C2–H7	1.088	1.093 ± 0.008	1.078	1.079	1.082	1.076	1.087
C2–H9	1.092	1.093 ± 0.008	1.082	1.082	1.089	1.085	1.100
C1–C3–H6	128.1	128.4 ± 0.2	131.4	130.8	125.6	124.6	126.2
H7–C2–H9	114.1	115.6	114.0	114.0	113.7	114.3	114.0
C1–C2–C3	60.2	60.0	59.0	59.1	69.7	69.4	68.7
C2–C1–H5	129.6	130.4	130.5	130.3	126.7	126.0	126.6
C2–c–C4	122.4	122.7 ± 0.5	120.6	121.0	133.2	133.8	133.5
c–C2–H7	121.6	122.9 ± 0.8	121.4	121.3	125.3	126.9	127.6
c-C2–H9	124.4	121.6 ± 0.9	124.7	124.6	121.0	118.8	118.3

[a] The center of the C1–C3 bond is designated as "c".

Table IV. CIS Vertical Transition Energies for Bicyclo[1.1.0]butane (eV) Calculated at MP2/6-31G* Geometry

trans	basis set 6-31G*	6-31+G*	6-31+G**	6-311+G*	6-311++G*	6-311++G(2d)	6-311(2+)G*	MP2/6-311(2+)G*
1	A_1, 9.56	A_1, 7.16	A_1, 7.13	A_1, 7.10	A_1, 6.85	A_1, 6.86	A_1, 6.79	A_1, 6.61
2	B_1, 9.90	B_1, 7.47	B_1, 7.45	B_1, 7.48	A_1, 7.28	A_1, 7.28	A_1, 7.16	A_1, 6.88
3	B_1, 10.74	A_1, 7.67	A_1, 7.65	A_1, 7.60	B_1, 7.34	B_1, 7.34	B_1, 7.19	B_1, 7.00
4	B_2, 11.02	B_2, 7.75	B_2, 7.73	B_2, 7.75	B_2, 7.52	B_2, 7.53	B_2, 7.38	B_2, 7.00
5	A_1, 11.07	B_1, 8.79	B_1, 8.76	B_1, 8.73	A_1, 8.50	A_1, 8.50	B_1, 8.10	A_1, 7.66
6	B_2, 11.30	A_1, 8.97	A_1, 8.94	A_1, 8.86	B_2, 8.67	B_1, 8.64	A_1, 8.11	B_1, 7.73
E (g)	−154.87082	−154.87395	−154.88454	−154.89867	−154.89878	−154.89979	−154.89873	−155.45386

two highest occupied MO's (ϕ_{14} and ϕ_{15}) and the four lowest virtual MO's calculated at the 6-311(2+)G* level of theory are shown in Figure 8. The higher occupied MO's change neither energy nor shape to a significant extent with increasing basis set size. However, the virtual orbitals are strongly affected in both energy and shape[12] by the inclusion of diffuse orbitals, and with two sets of these orbitals, many of the virtual orbitals have essentially the same energy which is close to zero.

The quantities of interest in the present context are, of course, not the orbital energies but the transition energies. We have chosen to do the calculations at the MP2/6-31G* geometry which is close to the experimental geometry (Table III). Excitation energies were first computed with the CI-singles method (CIS)[13] and several different basis sets. Here, the ground state is represented by the Hartree–Fock (HF) determinant while various excited states are expressed as the linear combinations of all possible determinants formed by replacing a single occupied orbital with an unoccupied orbital. The coefficients of these linear combinations are found as the eigenvectors of the complete Hamiltonian matrix, truncated to single substitutions. By using this technique, it is possible to calculate an excited state wave function for a state of the same symmetry as the ground state without variational collapse to the HF state. Energies computed are variational in the space of single substitutions and size-consistent, and they include some of the effects of electron correlation via the mixing of different excited determinants.

It was found that inclusion of either diffuse or polarization functions at the hydrogens had very little effect on the calculated transition energies. Diffuse functions at the carbons played a major role in determining the calculated transition energies (Table IV) and the use of two sets of diffuse functions at carbon (indicated by 2+) was particularly effective. All of the basis sets lead to agreement on the assignment of the first transition as A_1. The larger basis sets indicated that a second A_1 state and a B_1 state should have essentially the same energy, and both probably contribute to the strong band centered at 53 000 cm^{-1}. Recent calculations by Bent and Rossi have reached the same conclusion.[14] The first 20 calculated transitions obtained at the CIS/6-311-(2+)G* level are given in Table V.

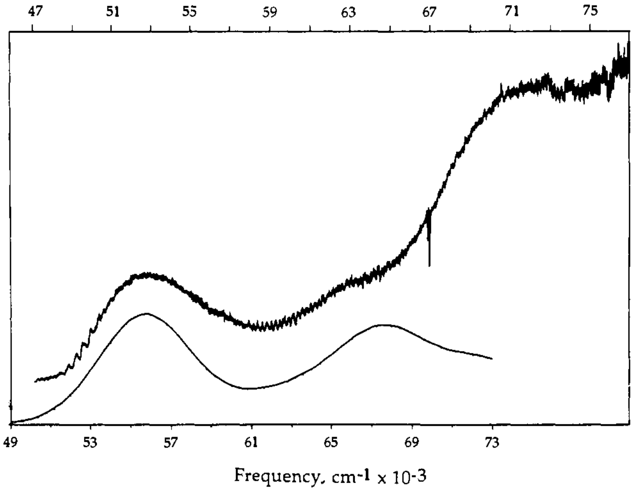


Figure 9. Calculated spectrum of bicyclobutane. The lower scale is for the calculated spectrum and the upper scale is for the observed spectrum.

It is possible to correct the transition energies further for the effects of electronic correlation by employing the Møller–Plesset perturbation theory to second order.[13] Here, the ground-state energy is computed by the traditional MP2 expression (approximating the effects of mixing double substitutions into the ground state) and the excited-state CIS energy is computed by an expression which approximates the mixing of double and triple substitutions into the excited state. The energies for the first six

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[13] Foresman, J. B.; Head-Gordon, M.; Frisch, M. J.; Pople, J. A. Submitted for publication.

[14] Bent, G. D.; Rossi, A. R. *J. Phys. Chem.* Submitted for publication.

Table V. Vertical Transition Energies and Intensities Calculated at the CIS/6-311(2+)G* Level

			CIS			CIS-MP2		
no.	assign	type	$cm^{-1} \times 10^{-3}$	eV	osc. strength	$cm^{-1} \times 10^{-3}$	eV	obs, eV
1	$2A_1$	1s	54.78	6.79	0.0005	53.32	6.61	~6.1
2	$3A_1$	$2p_z$	57.73	7.16	0.0451	55.50	6.88	6.6
3	$1B_1$	$2p_x$	58.03	7.19	0.0426	56.48	7.00	
4	$1B_2$	$2p_y$	59.54	7.38	0.0001	56.50	7.00	
5	$2B_1$	$3d_{xz}$	65.30	8.10	0.0046	62.35	7.73	
6	$4A_1$	$3d_{z^2}$	65.39	8.11	0.0009	61.77	7.66	
7	$2B_2$	$3d_{yz}$	65.57	8.13	0.0113	61.79	7.66	
8	$1A_2$	$3d_{xy}$	65.57	8.13	0.0000			
9	$5A_1$	$3d_{x^2-y^2}$	65.93	8.17	0.0022	62.16	7.71	
10	$6A_1$	$s + 3d_{z^2}$	68.28	8.47	0.0004			
11	$3B_1$	$3p_x$	69.14	8.57	0.0103	65.30	8.10	
12	$3B_2$	$3p_y$	69.66	8.64	0.0005			
13	$7A_1$	$4d_{z^2}$	69.78	8.65	0.0144	65.75	8.15	
14	$4B_1$	$4f_{x(x^2-3y^2)}$	70.57	8.75	0.0617	68.23	8.46	
15	$2A_2$	$4f_{xyz}$	71.54	8.87	0.0000			
16	$4B_2$	$4f_{y(3x^2-y^2)}$	71.70	8.89	0.0000			
17[a]	$3A_2$	1s	73.44	9.11	0.0000			
18	$5B_1$	$5f_{x(x^2-3y^2)}$	74.32	9.22	0.0468	73.13	9.07	
19	$8A_1$	$4f_{z^3}$	74.89	9.28	0.0003			
20[a]	$4A_2$	$2p_z$	75.95	9.42	0.0000			

[a] These states originate from ϕ_{14} rather than ϕ_{15}.

Table VI. Calculated Vibrational Frequencies for the Ground and $2A_1$ States of Bicyclobutane, 6-31+G*

		ground state			$2A_1$ excited state		
mode		calc	obs	sf	calc	scaled	obs
A_1	1	3434	3131	0.91	3286	2996	
	2	3339	3043	0.91	3218	2933	
	3	3246	2935	0.90	3162	2859	
	4	1676	1501	0.90	1588	1422	
	5	1410	1266	0.90	1256	1128	
	6	1205	1081	0.90	1174	1053	994
	7	945	839	0.89	977	867	
	8	791	657	0.83	700	581	622
	9	470	423	0.90	487	438	419

Table VII. Symmetries of Atomic Orbitals under C_{2v}

species	atomic orbitals
A_1	$s, p_z, d_{z^2}, d_{x^2-y^2}, f_{z^3}, f_{z(x^2-y^2)}$
A_2	d_{xy}, f_{xyz}
B_1	$p_x, d_{xz}, f_{xz^2}, f_{x(x^2-3y^2)}$
B_2	$p_y, d_{yz}, f_{yz^2}, f_{y(3x^2-y^2)}$

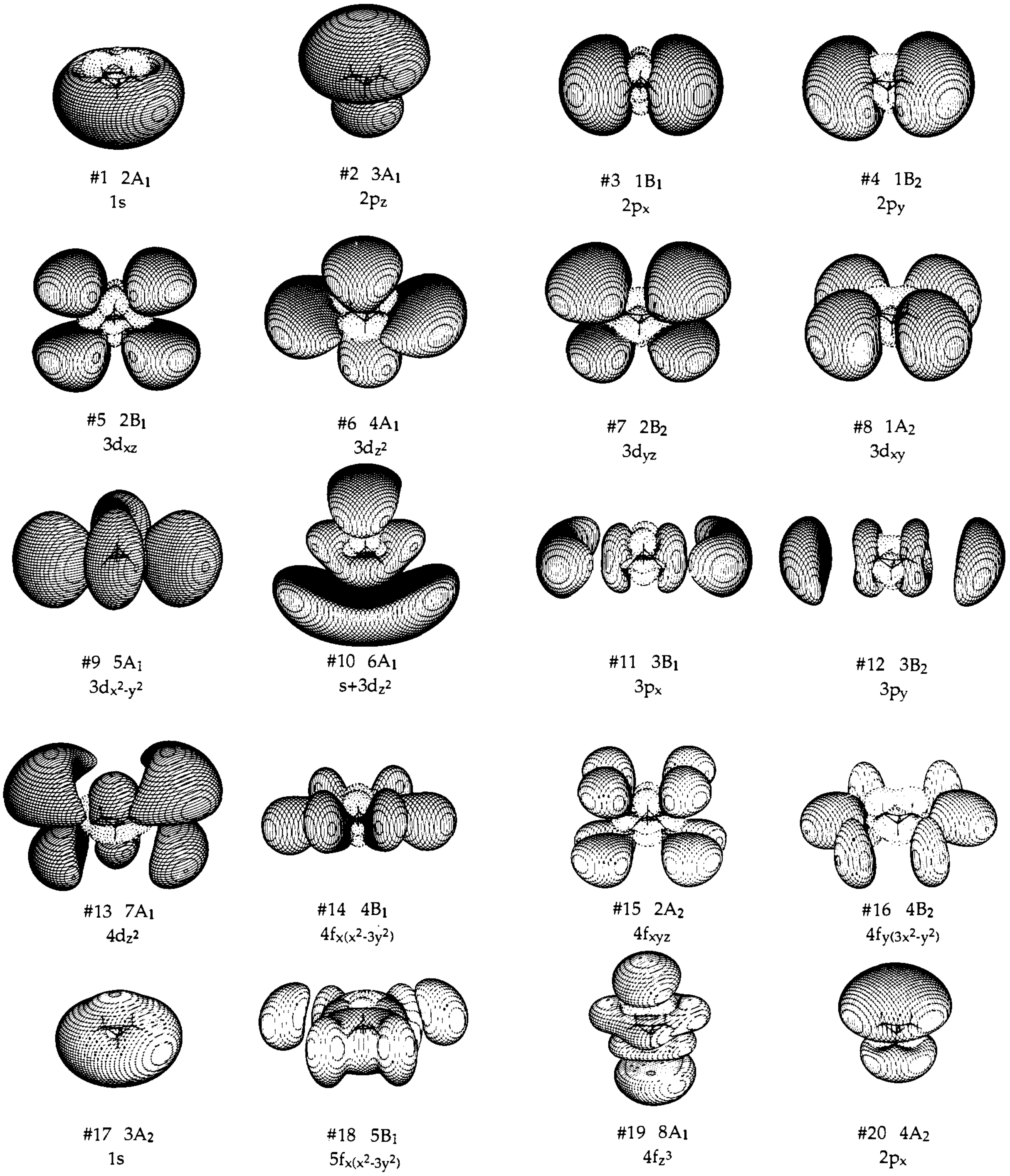
transitions are compared with the CIS transition energies in Table IV. The MP2-CIS/6-311(2+)G* energies for a number of the states are shown in Table V. Correction for electron correlation has a larger effect on the excited states than the ground state, and the calculated transition energies are somewhat reduced. However, they are still 0.4–0.5 eV too high. It is likely that a higher level of correction for electron correlation would be needed to reduce this difference. A spectrum derived by convoluting the calculated band centers with a Gaussian function is shown in Figure 9. It gives a reasonable agreement with the observed spectrum except for a systematic shift to higher frequencies (~ 2000 cm^{-1}). The higher observed intensity above 70 000 cm^{-1} probably results from excited states beyond those calculated in this study. The total oscillator strength for one electron should be close to unity, and the sum for the 20 calculated states is only 0.24.

We were particularly interested in knowing the geometry change on going to the $\tilde{A}$ ($2A_1$) state and the vibrational frequencies for this state. An optimized excited-state structure was obtained by using analytical gradient procedures[13] available for CIS wave functions. Excited-state frequency analysis was performed on the optimized structure by using numerical differentiation of these analytically computed gradients to obtain the second derivative of the wave function. The geometry calculated via CIS/6-31+G* is given in Table III, and it can be seen that the main effects are a lengthening of the central C–C bond and a flattening of the rings. The same effects are seen in the geometry of the radical cation and the two structures are remarkably similar. The vibrational frequencies for the excited state are compared with the ground-state frequencies in Table VI. The scaling factors (sf) are the ratios of the observed to calculated frequencies for the ground state. Since the excited-state frequencies were calculated to be similar to those for the ground state, the same scaling factors were applied to the calculated excited-state frequencies. The values thus obtained for ν_6, ν_8, and ν_9 are in very good agreement with those observed in the experimental spectrum. One may then have confidence that the frequencies calculated in this manner are satisfactory. It can be seen that the calculations for the $2A_1$ state and the experimental observations for the $\tilde{A}$ state are in remarkably good agreement.

The symmetries of the excited states are readily obtained, but each symmetry species corresponds to several different types of Rydberg states (Table VII). To gain additional information concerning the first transitions, the charge density distributions were calculated, and the differences from the ground-state distribution were obtained. They were first obtained by using the one-particle density matrix that is obtained as part of the CIS calculation. Contour plots of the charge density differences are shown in Figure 10. It can be seen that the shapes are remarkably similar to the atomic orbitals, with s, p, d, and f components being easily recognized (Figure 11). States 3 and 11 clearly correspond to $2p_x$ and $3p_x$ functions, respectively. The symmetries of atomic orbitals under C_{2v} are given in Table VII, and the assignments of the atomic orbital types for the excited states are given in Table V. Here, the quantum numbers correspond to the nodal character of the new charge distribution in the excited states. The conventional Rydberg assignment would start with $n = 3$.

In this set, states 1 and 17 and states 2 and 20 appear quite similar. The difference is that whereas most of the states originate from ϕ_{15} of the ground state, both 17 and 20 originate mainly from ϕ_{14}. Thus, they constitute the beginnings of another series of states related to the second ionization potential. The MO components of each of the exited states are available as supplementary material.

It also is possible to calculate the generalized (two particle) density matrix which yields multipole moments that are the correct analytical derivatives of the energy.[13] It was of interest to compare the charge density shifts derived from the one- and two-particle density matrices, and the latter were calculated for the first three excited states. The charge density difference plots are shown in Figure 12. Qualitatively, the changes in charge density are similar, but quantitatively, it can be seen that the two-particle density matrix yields less extreme changes in charge density in the region near the center core. At larger distances, the two density matrices give essentially the same results. It also was of interest to compare the charge density difference for the core region with


#1 $2A_1$ 1s

#2 $3A_1$ $2p_z$

#3 $1B_1$ $2p_x$

#4 $1B_2$ $2p_y$

#5 $2B_1$ $3d_{xz}$

#6 $4A_1$ $3d_{z^2}$

#7 $2B_2$ $3d_{yz}$

#8 $1A_2$ $3d_{xy}$

#9 $5A_1$ $3d_{x^2-y^2}$

#10 $6A_1$ $s+3d_{z^2}$

#11 $3B_1$ $3p_x$

#12 $3B_2$ $3p_y$

#13 $7A_1$ $4d_{z^2}$

#14 $4B_1$ $4f_{x(x^2-3y^2)}$

#15 $2A_2$ $4f_{xyz}$

#16 $4B_2$ $4f_{y(3x^2-y^2)}$

#17 $3A_2$ 1s

#18 $5B_1$ $5f_{x(x^2-3y^2)}$

#19 $8A_1$ $4f_{z^3}$

#20 $4A_2$ $2p_x$

Figure 10. Charge density difference plots for going from the ground state to the vertical excited states. The solid contours indicate regions where the charge density is increased in the excited state. The contour level was 1×10^{-4} e/B^3 for all except #13 and #18 where it was 5×10^{-5}. The structure of the molecule was drawn to scale and is the same for each state. In most cases the central C–C bond is down and perpendicular to the plane of the paper, but with #3, 5, 9, 10, 11, 14, 15 and 18 it is in the plane of the paper.

that for the radical cation less the parent molecule. This is shown in Figure 13. It can be seen that they are essentially the same. Although the core region of the excited states changes a little from one symmetry group to another, all of the excited states can be well described as a radical cation plus one electron in a diffuse orbital.

The charge density distribution clearly indicates that all of the excited states of bicyclobutane are of the same type and are best described as Rydberg transitions. An interesting question is why some of the transitions have a relatively large calculated and observed oscillator strength whereas most have very little intensity. If one looks at MO 15 down the y axis (Figure 14), it has the characteristic of a d orbital. If the atomic selection rules applied, one would expect the more intense transition to correspond to $\Delta l = \pm 1$. Transitions to a p-type orbital should then be relatively intense, as is found to be the case.

V. Triplet States. It has been suggested that triplet states should have less Rydberg character than singlet states.[15] One reason for Rydberg character in the singlet excited states is the requirement for orthogonality with the ground state, which is more easily achieved if the two states occupy different regions of space. The triplet does not have this problem since the electron spins are orthogonal. Therefore we have examined the first three triplet states using the CIS procedure and the 6-311(2+)G* basis set.

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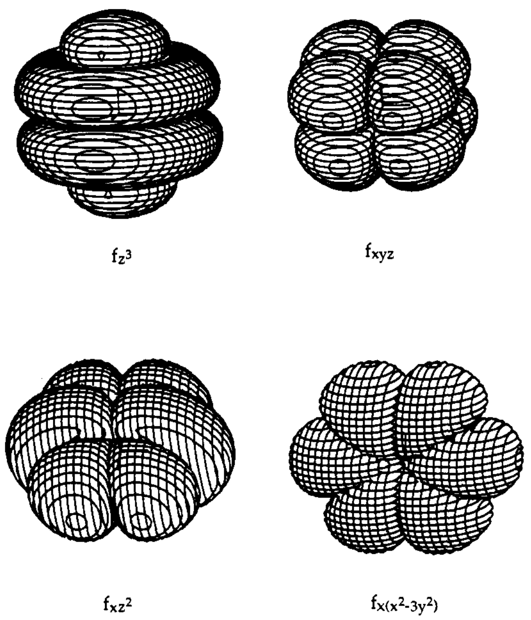
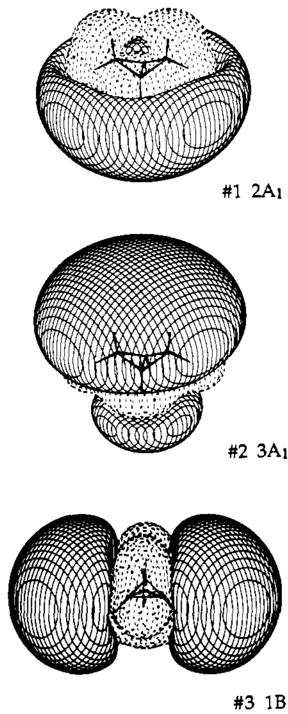
(15) Robin, M., ref 11, p 154. Bender, C. F.; Dunning, T. H., Jr.; Schaefer, H. F., III; Goddard, W. A., III; Hunt, W. J. *Chem. Phys. Lett.* **1972**, *15*, 171.



f_{z^3} f_{xyz}

f_{xz^2} $f_{x(x^2-3y^2)}$

Figure 11. Charge density plots for f atomic orbitals.



#1 $2A_1$

#2 $3A_1$

#3 $1B_1$

Figure 12. Charge density difference plots for going from the ground state to the first three vertical excited states based on the generalized (two-particle) density matrix. The contour level was 1×10^{-4} e/B^3.

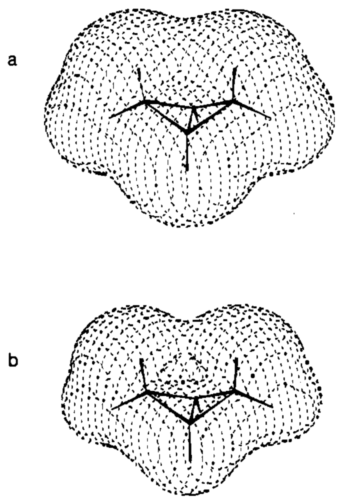


Figure 13. Charge density depletion plots for (a) the radical cation compared to the parent hydrocarbon with the 6-311(2+)G* basis and (b) the core region of the $2A_1$ excited state of bicyclobutane (2-particle density matrix). The contour level was 1×10^{-4} e/B^3.

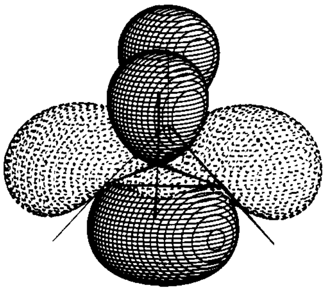
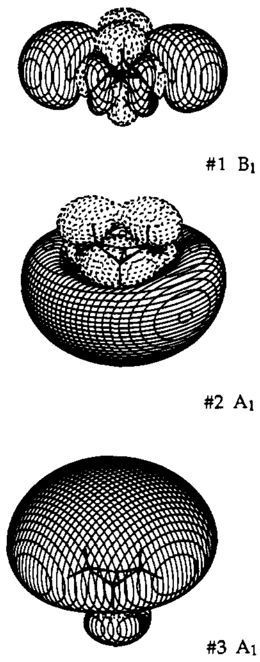


Figure 14. Molecular orbital 15 looking down the *y* axis showing its d-like character.



#1 B_1

#2 A_1

#3 A_1

Figure 15. Charge density difference plots for going from the ground state to the first three vertical triplet states based on the one-particle density matrix. The contour level was 1×10^{-4} e/B^3.

The calculated vertical transition energies were ($^3B_1$) 6.58 eV, ($^3A_1$) 6.66 eV, and ($^3A_1$) 6.95 eV. The calculated changes *in* charge density for going from the ground state to the triplet states are shown in Figure 15. The $^3A_1$ states are similar to the $^1A_1$ states. The long dimensions for the 1×10^{-4} e/B^3 contours were 10.8 and 11.6 Å for the $2A_1$ and $3A_1$ states and 9.0 Å for the $^3A_1$ state with use of the one-particle density matrix. Thus, this triplet state is slightly less diffuse than the corresponding singlet states. The $^3B_1$ state may at first appear different than the $^1B_1$ state, but that mainly results from the smaller spatial extent of the triplet state. Here, the long dimension for the $1B_1$ state is 13.5 Å whereas for the $^3B_1$ state it is 9.2 Å. The vertical triplet states do resemble the singlet states and are somewhat less diffuse. It may be noted that whereas the "size" of the singlet states decreases slightly with the two-particle density matrix (9.5, 10.2, and 12.1 Å for the $2A_1$, $3A_1$, and $1B_1$ states), no change was found for the $^3B_1$ state.

It also was of interest to see if the relaxed triplet states resemble the relaxed singlet states. Therefore we have carried out geometry optimizations for the two lowest energy triplet states using the CIS formalism and also have carried out UHF and UMP2 ge-

Table VIII. Calculated Structures for Bicyclo[1.1.0]butane Ground State and Triplet States

	ground state	$^3A_1$ state	$^3B_1$ state		
parameter[a]	MP2/6-31+G*	CIS/6-31+G*	UHF/6-31+G*	UMP2/6-31+G*	CIS/6-31+G*
C1–C3	1.503	1.679	2.075	2.063	2.078
C1–C2	1.494	1.475	1.517	1.510	1.517
C1–H5	1.081	1.096	1.075	1.085	1.075
C2–H7	1.089	1.083	1.092	1.104	1.088
C2–H9	1.093	1.089	1.090	1.101	1.090
C1–C3–H6	127.1	122.8	167.2	169.4	158.6
H7–C2–H9	114.3	114.1	107.4	106.7	107.7
C1–C2–C3	60.4	69.4	86.3	86.2	86.5
C2–C1–H5	129.3	126.0	131.2	131.7	129.2
C2–c-C4	122.7	132.3	174.3	174.4	177.3
c-C2–H7	121.7	124.8	125.4	125.5	127.0
c-C2–H9	124.1	121.1	127.2	127.8	125.3
energy	−155.41852	−154.64264	−154.84088	−155.32893	−154.82141[b]

[a] The center of the C1–C3 bond is designated as "c". The numbering of the atoms is shown in Table III. [b] Almost converged geometry.

ometry optimizations for the lowest energy triplet. The results are shown in Table VIII. The $^3A_1$ state has a geometry which is close to that for the first $^1A_1$ excited state. However, the geometry of the $^3B_1$ state is markedly different. Here, the molecule has become almost planar with the angle between the three-membered rings about 175°, and the central bond length has increased from 1.50 Å in the ground state to 2.08 Å. It resembles a slightly puckered cyclobutane-1,3-diyl. The reasons for the difference in structure for the first two triplet excited states continues to be examined. One effect is to markedly lower the adiabatic excitation energy for going to the $^3B_1$ state to 2.44 eV (MP2/6-31+G*), which is close to a normal C–C bond energy.

Conclusions

Theory and experiment now provide consistent results concerning the identity and electronic nature of the Ã state of bicyclobutane. The CIS calculations find that the Ã state has A_1 symmetry. This result is supported by the observation of the same vibrational bands one- and two-photon transitions, indicating it is an electric-dipole allowed transition in both cases, as would be the case for an A_1 state. The properties of the Ã state strongly suggest that it is a 3s Rydberg state. Such a state would be expected to have A_1 symmetry, which is again consistent with the theoretical results. The vibrational bands in the spectra of bicyclobutane-d_0, -d_2, and -d_4 have been reassigned with the aid of a vibrationally cooled molecular beam spectrum of bicyclobutane and the known isotopic shifts in the ground state. Progressions in the totally symmetric mode, ν_9, dominate all three spectra. This is consistent with the strong similarity between the calculated excited state geometry and the ν_9 normal mode composition. The observed transition energy, calculated charge distribution, and similarity of the excited-state structure to that of the radical cation all agree that the excited state is an s Rydberg state.

The CIS calculations show that all of the electronically excited states are quite similar and are best described as Rydberg states. The calculated spectrum is in quite good accord with the observed spectrum. The calculated structure of the Ã state was found to be rather similar to that of the bicyclobutane radical cation, and the calculated vibrational frequencies were found to be in good agreement with the observed frequencies.

Calculations. The ab initio calculations were carried out with GAUSSIAN-90.[16] The density matrices produced with this program were transformed into natural orbitals, and charge densities were calculated for both 20 and 40 au cubes with use of 80 points in each direction. The differences in charge densities on going from the ground state to each of the excited states were calculated, and contour plots were prepared by a modification of the program of Jorgensen.[17] Standard basis sets were used except for the double diffuse set (2+) which was the standard 6-311+G* (6d) basis set with an extra sp shell with an exponent of 0.0131928.

Acknowledgment. This investigation was supported by a grant from the National Science Foundation. C.M.H. thanks the Fannie and John Hertz Foundation for a predoctoral fellowship. We thank Prof. William A. Chupka for helpful discussion on Rydberg states, Dr. Michael J. Frisch for his assistance with the excited-state calculations, and Mr. Dan Severance for his assistance with the 3-D plotting programs. Some of the calculations were carried out at The Pittsburgh Supercomputing Center with the aid of a grant from that center.

Registry No. 1, 157-33-5.

Supplementary Material Available: Listing of assignments of the vibrational modes for bicyclobutane-d_2 and -d_4 as well as the description of the excited states in terms of their MO components (5 pages). Ordering information is given on any current masthead page.

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