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Analysis of the high-resolution infrared spectrum of cyclopropane

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ABSTRACT

The high-resolution infrared spectrum of cyclopropane (C_3H_6) has been measured from 100 cm^{-1} to 2200 cm^{-1}. In that region we have identified 24 absorption bands attributed to six fundamental bands, five combination bands, three hot bands and 10 difference bands. Long pathlength spectra, up to 32 m, facilitated the identification and analysis of many previously unstudied infrared inactive, and Raman and infrared inactive vibrational states, including direct access to two forbidden fundamental states, ν_4 and ν_{14}. An improved set of constants for the ground vibrational state as well as for the fundamental vibrations ν_7, ν_9, ν_{10}, ν_{11} are also reported. The spectral resolution of the measurements varied from 0.002 cm^{-1} to 0.004 cm^{-1}.

1. Introduction

The concepts of molecular strain, structure, stability and reactivity represent some of the major areas of study in chemistry. Carbon, more than any other element in the periodic table, boasts a versatility unmatched in regards to the strength, angle and shape with which it forms bonds. Cyclic and caged forms of carbon based molecules abound and possess a wide range of unusual and unprecedented chemical properties [1]. Strained carbon compounds are finding ever more applicability in industry, material science and medicine [2]. Cyclopropane is the simplest, yet most highly strained small ring cyclic hydrocarbon. Early investigations into the chemistry and spectroscopy of cyclopropane were focused around determining the nature of the unusual 60° C—C bond angle, research that inspired both Coulson and Moffitt's "banana bond" theory [3] as well as Walsh's sp^2 hybridized orbital model [4] for describing strained organic compounds.

The first infrared study on cyclopropane with sufficient resolution to obtain rotational constants for the ground vibrational state as well as for a number of fundamental vibrational states was conducted by Duncan [5] in 1968. The $\nu_5 + \nu_{10}$ band of cyclopropane was later used by Maki [6] to verify the predictions of Cartwright and Mills [7] on the effect of *l*-resonance perturbations. Shortly thereafter, Butcher and Jones [8] recorded Raman spectra with an argon ion laser at 0.3–0.5 cm^{-1} resolution and confirmed the earlier suspicions of Mathai [9] that Fermi resonance interactions with overtone vibrations plagued a number of fundamental vibrational states. Since then, Plíva et al. published a series of papers [10–16] on high-resolution infrared and inverse Raman spectra of cyclopropane. Though this series of papers represents the most thorough study yet on cyclopropane, the analysis of the rovibrational states was hampered in many cases by interactions with several infrared inactive and infrared and Raman inactive vibrational states.

To fully account for these perturbations and to elucidate the rovibrational parameters for many other infrared inactive and infrared and Raman inactive vibrational states, all fundamental vibrational modes with band origins that fall below 2200 cm^{-1} have been recorded and analyzed using either transitions that directly accessed the rovibrational levels or that indirectly sensed the levels through a rotational perturbation. In the present work, ten fundamental vibrational states have been characterized as well as several overtone and combination states. The modes, symmetries, activities and deperturbed vibrational band origins for the fourteen fundamental vibrations of cyclopropane are given in Table 1. Even though the majority of the infrared spectra were recorded at approximately the same resolution (~0.002 cm^{-1}) as in Plíva's work, the current analysis benefits from the utilization of a long pathlength (up to 32 m) White cell which allowed for the extension of the analysis of many vibrational bands to higher *J* and *K* levels as well as facilitated the identification of hot band transitions. The most novel aspect of this examination, however, was the recording and analysis of difference band spectra which aided the identification and analysis of many infrared inactive, and Raman and infrared inactive vibrational states.

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Table 1
The modes, symmetries, spectral activity, and deperturbed vibrational states for C_3H_6.

Normal mode	Symmetry	Activity	$G(\upsilon,l)$ (cm^{-1})
ν_1	A_1'	R	3026.7[a]
ν_2	A_1'	R	1499.3[b,c]
ν_3	A_1'	R	1189.2
ν_4	A_1''	–	1126.7
ν_5	A_2'	–	1066.8
ν_6	A_2''	IR	3101.7[d]
ν_7	A_2''	IR	854.0
ν_8	E'	IR/R	3019.2[e]
ν_9	E'	IR/R	1440.0[b,f]
ν_{10}	E'	IR/R	1028.4
ν_{11}	E'	IR/R	868.4
ν_{12}	E''	R	3082.0[g]
ν_{13}	E''	R	1191.3
ν_{14}	E''	R	737.5

[a] Ref. [16].
[b] Deperturbed values.
[c] The resonance with $2\nu_{14}^0$ shifts the band center up to 1505.4 cm^{-1}.
[d] Ref. [15].
[e] Ref. [10].
[f] The resonance with $2\nu_{14}^2$ shifts the band center down to 1437.3 cm^{-1}.
[g] Ref. [8].

Table 2
Parameters describing the spectra used in these measurements.

Region (cm^{-1})	Pathlength (m)	Pressure (Torr)	Resolution (cm^{-1})	Calibration gas
35–380	32	10.4	0.004	H_2O[a]
200–700	35.2	10.8	0.0035	OCS[b]
450–800	32	11.0	0.0035	OCS
600–830	32	9.0	0.0025	OCS
600–1000	3.2	0.9	0.0020	OCS
	12.8	0.8		
800–1200	0.20	2.0	0.0025	OCS
900–1250	3.2	0.08	0.0020	OCS
	12.8	0.8		
1200–1680	6.4	0.2	0.0020	N_2O
	19.2	0.37	0.0020	
	19.2	1.01	0.0020	
1600–2100	0.7	6.4	0.0025	NO
	1.0	12.8	0.0025	
2000–2500	1.0	12.8	0.003	OCS

[a] Ref. [18].
[b] OCS, N_2O and NO from Ref. [19].

2. Experimental details

The spectra were recorded using Bruker IFS 120HR and 125HR Fourier transform infrared spectrometers located at the PNNL facilities. The samples were recorded at room temperature in a variable pathlength White cell, with instrumental resolution ranging between 0.0020 and 0.0040 cm^{-1}. Specific parameters for a given spectral region are listed in Table 2. A Globar light source and either a liquid helium cooled Si-bolometer or a liquid nitrogen cooled HgCdTd detector were used. A 6 mm Mylar beam splitter was used in conjunction with the Si-bolometer, and a KBr beamsplitter was used in with the HgCdTd detector. The resulting absolute wavelength calibration is estimated to be ±0.0002 cm^{-1}. Further details on this system can be found in Ref. [17]. Lecture bottles of cyclopropane were purchased from Matheson and were used without further purification.

3. Analysis of the spectra

3.1. Some general considerations

Cyclopropane has D_{3h}point group symmetry, where dipole vibrational transitions are only allowed for states where the direct product of the upper and lower vibrational states is of either A_2'' or E' symmetry. In this work we have also observed two vibrational transitions from the ground state, 4_0^1 and $14_{0,0}^{1,1}$, which do not fulfill this requirement. For Raman transitions, this product must be of A_1' or E'' symmetry. With nine atoms and an A_1' ground vibrational state, cyclopropane possesses 14 fundamental vibrational modes of symmetry species $3A_1'$ (R) $\oplus$ A_1'' (−) $\oplus$ A_2' (−) $\oplus$ $2A_2''$ (IR) $\oplus$ $4E'$ (IR) $\oplus$ $3E''$ (R). Of the six fundamental infrared-allowed vibrational bands, only four occur in the region of interest, 100–2200 cm^{-1}, and are shown in Fig. 1. Six additional fundamental states were accessed through difference bands where the lower vibrational states possess symmetry other than A_1'. Some of those bands are displayed in Figs. 2 and 3 where the lower traces in the figure are the calculated spectra for the difference bands at approximately the correct relative intensities. Because these transitions originate from states with symmetry other than A_1' and the electric dipole selection rules for the rovibrational transitions still apply, the difference band spectra exhibit a variety of unusual transition patterns not normally observed in a molecule of this symmetry.

As opposed to both BF_3 and SO_3, which are two prototypical D_{3h} point group molecules, where certain rovibrational symmetry levels are not statistically allowed, the spin statistics of C_3H_6 are such that no symmetry exclusions occur. One consequence of this is observed in the A_1–A_2 splitting in some $K > 0$ levels. In contrast to both BF_3 and SO_3 where splitting of the rovibrational pair manifests itself as a pseudo-splitting, where only one member of the A_1–A_2 partner is actually observed in the spectrum, both pairs are observed in C_3H_6. In addition, $K = 0$ rotational levels in the ground vibrational state are allowed for both even and odd values of J, whereas in $BF_3(SO_3)$ the even(odd) J rotational levels are not allowed due to exclusion of the $A_1(A_2)$ rotational levels. The spin statistical weights for the rotational levels of C_3H_6 in states of different vibrational symmetry are given in Table 3.

The vibrational nomenclature is the same as that used by Plíva et al. [10–16]. The conventions and nomenclature for the various matrix elements and rovibrational constants are the same as that described in previous work by the authors on both $^{10}BF_3$ and $^{11}BF_3$ [20–23] and a variety of SO_3 isotopomers [17,24–27]. Because cyclopropane has several normal vibrational modes, we are using in many places the Brand, Callomon, Watson (BCW) symbolism for denoting the vibrational states and transitions [28–30]. For vibrational states this notation has the form: $(\text{vib. }\#i^{vi,li}\ \text{vib. }\#j^{vj,lj}\ldots)^l$. With this notation, only the vibrational numbers are given for those normal modes with non-zero quanta. The superscripts within the parentheses denote first the number of quanta of each normal vibrational mode followed, if it is a degenerate mode, by the quantum number for vibrational angular momentum for that mode. The parentheses and the superscript outside the parentheses are not necessary if no degenerate vibrations are involved or if the resulting value of l is unambiguous. The superscript outside of the parentheses denotes the total vibrational angular momentum given by $l = \sum_i l_i$. For transitions between vibrational states the notation is similar except that the lower state quantum numbers are shown as subscripts so that, for instance, the difference transition $\nu_{13}-\nu_{14}$ would be shown as $(13_{0,0}^{1,1}14_{1,1}^{0,0})_1^1$. However, in this case since the total vibrational angular momentum, l, is obvious, the parentheses and super- and subscripts outside the parentheses, are not needed. In some cases, as an aid to the reader, we will use both the ν_i notation as well as the BCW notation.

3.2. Description of the spectral analysis

The Hamiltonian for an oblate symmetric top is given in Papousek and Aliev [31] and other texts. Also helpful in describing the interaction terms affecting the rovibrational levels in this work are papers by DiLauro and Mills [32], and Cartwright and Mills