High-resolution infrared spectra of spiropentane, C_5H_8

J.E. Price [a], K.A. Coulterpark [a], T. Masiello [b], J.W. Nibler [a,*], A. Weber [c], A. Maki [d], T.A. Blake [e]

[a] Department of Chemistry, Oregon State University, Corvallis, OR 97332-4003, United States
[b] Department of Chemistry and Biochemistry, California State University, East Bay, Hayward, CA 94542, United States
[c] Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States
[d] 15012 24th Ave., S.E, Mill Creek, WA 98012, United States
[e] Pacific Northwest National Laboratory, P.O. Box 999, Mail Stop K8-88, Richland, WA 99352, United States

ABSTRACT

Infrared spectra of spiropentane (C_5H_8) have been recorded at a resolution (0.002 cm^{-1}) sufficient to resolve for the first time individual rovibrational lines. This initial report presents the ground state rotational constants for this molecule determined from the detailed analysis of the v_{16} (b_2) parallel band at 993 cm^{-1}. In addition, the determination included more than 2000 ground state combination-differences deduced from partial analyses of four other infrared-allowed bands, the $v_{24}(e)$ perpendicular band at 780 cm^{-1} and three (b_2) parallel bands at 1540 cm^{-1} (v_{14}), 1568 cm^{-1} ($v_5 + v_{16}$), and 2098 cm^{-1} ($v_5 + v_{14}$). In each of the latter four cases, the spectra show complications; in the case of v_{24}, these complications are due to rotational l-type doublings, and in the case of the parallel bands, the spectral complexities are due to Fermi resonance and Coriolis interactions of the upper states with nearby levels. The unraveling of these is underway but the assignment of many of these transitions permit the confident use of the ground state differences in determining the following constants for the ground state (in units of cm^{-1}): $B_0 = 0.1394741(1)$, $D_J = 2.461(1) \times 10^{-8}$, $D_{JK} = 8.69(3) \times 10^{-8}$. For the unperturbed v_{16} fundamental, more than 3000 transitions were fit and the band origin was found to be at 992.53793(3) cm^{-1}. The numbers in parentheses are the uncertainties (two standard deviations) in the value of the last digit of the constants. Surprisingly, the very accurate B_0 value measured here is *lower* than the value (0.1418 cm^{-1}) calculated from an electron diffraction structure, instead of being higher, as expected. Where possible, the rovibrational results are compared with those computed at the anharmonic level using the B3LYP density functional method with a cc-pVTZ basis set. These too suggest that the electron diffraction results are in question.

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1. Introduction

Recently, we have examined the high-resolution infrared spectra of several five-carbon strained ring compounds of high symmetry: propellane [1–3], bicyclopentane [4,5] and, in this work, spiropentane. The structures and symmetries of these are shown in Fig. 1. In all three cases, the molecules are of considerable interest to structural chemists because of their high ring strain and, in the case of propellane, because of the very unusual axial bond. All three molecules are symmetric tops and relatively small so it is rather surprising that none had previously been examined spectroscopically at a resolution sufficient to discern individual rovibrational transitions. In part, this may be due to the fact that none of these compounds is readily available from commercial sources. However synthesis methods for each have been published [6–8] and we have used these methods in preparing small amounts

of each compound with sufficient purity to yield excellent high-resolution infrared spectra.

A second motivation for studying these molecules comes from our interest in assessing the value of quantum calculations as an aid in analyzing the complex vibration–rotation spectral patterns one often observes in high-resolution spectroscopy. Such complexity occurs even for small molecules of high symmetry and it stems from changes in rotational constants with vibrational state and from Fermi resonance and Coriolis couplings between states. Estimates of the rovibrational parameters accounting for these effects are now available from more refined potential energy surface calculations by quantum mechanical methods. In particular, recent versions of the Gaussian quantum chemistry program [9] provide not only quadratic derivatives of the potential energy but also the cubic and quartic force constants required for use of perturbation expressions to estimate many rovibrational parameters. These then enable spectral simulations that are quite helpful in making initial quantum number assignments in complex spectra. Moreover, once accurate molecular

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* Corresponding author. Fax: +1 541 737 2062.
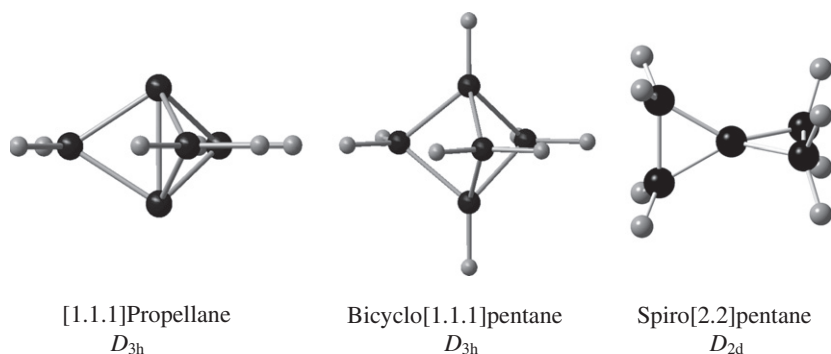 *E-mail address:* Niblerj@chem.orst.edu (J.W. Nibler).

Fig. 1. Structural arrangements for [1.1.1]propellane, bicyclo[1.1.1]pentane, and spiro[2.2]pentane.

parameters are determined from the spectral analysis, their values serve as added tests of the method and basis sets chosen in the quantum calculations. In this manner, for example, it has been determined that the Gaussian B3LYP density functional method applied to a cc-pVTZ basis set gives quite good rovibrational parameters at a reasonable investment of computer time. In addition, the calculations give helpful information about relative infrared and Raman band intensities that can further aid in spectral interpretations.

In the present study spiro[2.2]pentane (spiropentane) was examined using high-resolution infrared spectroscopy. Spiropentane was first synthesized by Gustavson [10] who suggested several possible structures for the compound with the empirical formula C_5H_8, but his structures were subject to controversy until the work by Murray and Stevenson [11], who isolated this species and gave a brief history of the earlier work. The prefix spiro (from the Greek for twist) was suggested by Baeyer [12] for the class of compounds in which smaller alkane ring compounds are fused by a common carbon atom. The simplest of these is spiropentane, formed by two cyclopropane rings joined at a common carbon atom where the planes of the two rings are twisted 90° with respect to one another [12], in accord with the valence orbitals of the common carbon atom (see Fig. 1).

The initial spectroscopic study by Murray and Stevenson [11] prompted a series of spectroscopic and structural studies of this molecule. Cleveland et al. [13] reported the results of the first study of the vibrational infrared and Raman spectra of spiropentane. Raman spectra of the liquid and infrared spectra of liquid and vapor phase spiropentane were obtained, including the values of the depolarization factors of the Raman lines, which enabled the assignments of the observed transitions to fundamental and combination bands.

A report on the thermodynamic studies of spiropentane by Scott et al. [14] lists the physical properties, heat capacities, vapor pressure, entropies, and thermodynamic functions of spiropentane and relates these data to the vibrational spectra. This work was followed by that of Burns and McGavin [15] who reinvestigated the Raman spectra of the liquid and the infrared spectra of vapor phase and low temperature solid spiropentane-H_8 with more modern instrumentation.

Structural investigations of spiropentane were carried out mainly by electron diffraction. The first of these was done by Rogowski [16], followed by those of Donohue et al. [17] and Dallinga et al. [18]. In addition, Buckingham et al. [19] and Bechthold and Goldstein [20] studied the NMR spectrum of spiropentane in an orienting liquid crystal, while Boese et al. [21] investigated crystalline spiropentane (mp = −115 °C) by X-ray diffraction. Among theoretical investigations are normal coordinate treatments reported by Cyvin and Gebhardt [22], Burns, McGavin, and Wong [23], who also predicted the vibrational frequencies of the perdeuterated species

C_5D_8, and Krainov and Sverdlov [24]. These computations largely relied on the transferability of force constants from cyclopropane. Lastly we mention some *ab initio* treatments whose results are related to those of experimental and normal coordinate studies. Thus, Schaad and Jarzęcki [25] report the results of their *ab initio* calculations of the vibrational frequencies and infrared spectra of spiropentane and its deuterated isotopomers, while Richard and Ball [26] calculated the thermodynamic properties, fundamental vibrational frequencies and intensities of spiropentane and its boron-containing derivatives by *ab initio* methods. Dodziuk, Leszcynski and Jackowski [27] used Hartree–Fock, Møller-Plesset2, and density functional methods with 6-31G** and 6-311++G** basis sets to calculate the vibrational frequencies and intensities, and structural parameters of spiropentane, spiropentene, and spiropentadiene, and correlated the results for spiropentane with those obtained by experimental methods.

Spiropentane is a prolate symmetric top with D_{2d} molecular symmetry; the only other D_{2d} molecules that have been examined at high spectroscopic resolution are allene [28] and cyclobutane [29]. In our current work on spiropentane, the fundamental ν_{16} b_2 parallel band near 990 cm^{-1} was analyzed in detail. In addition partial analyses were done for the ν_{24} e perpendicular band near 770 cm^{-1} and for several parallel bands for which evidence was seen of significant perturbations in the upper state level positions due to interaction with nearby energy states. Such complexity is not surprising because more Coriolis interactions are symmetry-allowed between vibrational states for a symmetric rotor of D_{2d} symmetry compared to one of D_{3h} symmetry. Moreover, the degenerate upper E levels for perpendicular bands such as ν_{24} are split by two different rotational l-doubling constants (q^+, q^-) rather than by one (q^+) as is the case for molecules of D_{3h} symmetry. Because of the spectral complexity caused by these interactions, the analysis of these bands is not yet complete; however the spectral assignments of many rovibrational transitions in these bands are sufficiently clear that these data were used in a combination-difference analysis to determine level spacings in the ground state. In total, 2111 such differences were deduced from four bands and these were combined with 3310 transitions of the unperturbed ν_{16} parallel band in obtaining the rovibrational parameters for both the ground and ν_{16} states. Parameters of the various other bands studied will be given in a separate publication.

2. Experimental details and results

2.1. Synthesis

Spiropentane was prepared by zinc reduction of pentaerythrityl tetrabromide, $C(CH_2Br)_4$, using the method of Applequist et al. [8]. Into a three-neck round bottom flask were placed 15.06 g of disodium ethylenediamine tetraacetate, 4.54 g sodium hydroxide,