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High resolution infrared spectroscopy of [1.1.1]propellane: The region of the ν_9 band

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ABSTRACT

The region of the infrared-active band of the ν_9 CH_2 bending mode [1.1.1]propellane has been recorded at a resolution (0.0025 cm^{-1}) sufficient to distinguish individual rovibrational lines. This region includes the partially overlapping bands ν_9 (e') = 1459 cm^{-1}, $2\nu_{18}$ ($l = 2$, E') = 1430 cm^{-1}, $\nu_6 + \nu_{12}$ (E') = 1489 cm^{-1}, and $\nu_4 + \nu_{15}$ (A_2'') = 1518 cm^{-1}. In addition, the difference band $\nu_4 - \nu_{15}$ (A_2'') was observed in the far infrared near 295 cm^{-1} and analyzed to give good constants for the upper ν_4 levels. The close proximities of the four bands in the ν_9 region suggest that Coriolis and Fermi resonance couplings could be significant and theoretical band parameters obtained from Gaussian *ab initio* calculations were helpful in guiding the band analyses. The analyses of all four bands were accomplished, based on our earlier report of ground state constants determined from combination differences involving more than 4000 pairs of transitions from five fundamental and four combination bands. This paper presents the analyses and the determination of the upper state constants of all four bands in the region of the ν_9 band. Complications were most evident in the $2\nu_{18}$ ($l = 2$, E') band, which showed significant perturbations due to mixing with the nearby $2\nu_{18}$ ($l = 0$, A_1') and $\nu_4 + \nu_{12}$ (E') levels which are either infrared inactive as transitions from the ground state, or, in the latter case, too weak to observe. These complications are discussed and a comparison of all molecular constants with those available from the *ab initio* calculations at the anharmonic level is presented.

1. Introduction

[1.1.1]Propellane (C_5H_6) [or, for brevity, propellane] is a molecule with most unusual bonding. The geometric structure is shown in Fig. 1, along with that of bicyclo[1.1.1]pentane (C_5H_8) in which the axial carbon atoms exhibit bonding in an expected, quasi-tetrahedral manner. This is in contrast to propellane in which the axially located carbon atoms are linked together by an "inverted bond", internal to the bi-pyramid. Previous spectroscopic work on propellane and references to the relevant extant literature were presented by us in earlier papers, as were the details of its synthesis and the experimental conditions under which the spectra were recorded [1,2]. The vibrational infrared and Raman spectra [3–6], and electron diffraction studies [7,8] of both molecules have established their geometrical shape, and the latter of these investigations have also provided accurate internuclear bond distances, especially those that describe the carbon–carbon bond lengths. Of special note are the separations of the axial carbon atoms, which are 1.58 Å for propellane and 1.88 Å for bicyclopentane, respectively, while the bond lengths between the axial and equatorial carbon atoms are 1.52 Å for propellane and 1.55 Å for bicyclopentane. The much shorter bond between the axial carbon atoms in propellane versus that in bicyclopentane suggests a significant effect on the rovibrational frequencies of its carbon skeleton as compared to those of bicyclopentane. One of the purposes of our investigations of these two molecules is to provide experimental rovibrational data to examine such effects.

The experimental studies were conducted in concert with Gaussian *ab initio* computations which, at the harmonic level, provide useful estimates of normal mode frequencies (ω's) and infrared/Raman intensities as well as Coriolis coupling constants. At the anharmonic level, the calculations give cubic and quartic force constants that yield helpful estimates of the anharmonic frequencies (ν's) and of ground state rotational B and C constants and their change when the normal modes are excited. These parameters proved to be an important aid in the various band analyses of both propellane and bicyclopentane, as described later. Our detailed investigation of bicyclopentane is the subject of forthcoming publications.

Propellane and bicyclopentane are appealing molecules for high resolution spectroscopic study since they are textbook examples of

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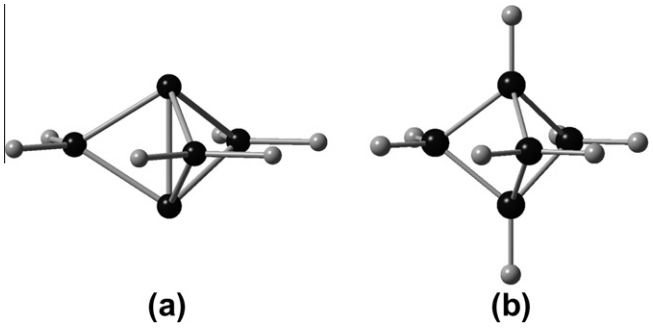

Fig. 1. Structures of (a) [1.1.1]propellane (C_5H_6) and (b) bicyclo[1.1.1]pentane (C_5H_8). Both molecules belong to the point group D_{3h} and the methylene groups lie in the σ_h plane.

symmetric tops, each having D_{3h} molecular symmetry. In both cases the molecule is an oblate rotor with the *C*-axis (about which the moment of inertia is larger) coinciding with the threefold symmetry axis. The 27 normal modes of propellane are distributed over the various species (irreducible representations) by the total vibrational representation

$$\Gamma_{vib} = 4a_1'(R) + 2a_2' + a_1'' + 2a_2''(IR) + 6e'(IR, R) + 3e''(R).$$

The letters in parentheses describe the infrared (IR) or Raman (R) selection rules for transitions from the ground state. The a_1' and e'' modes are Raman active only, the a_2'' modes are infrared active only, and the e' modes can give rise to both infrared absorption and Raman scattering spectra. The a_2' and a_1'' modes are inactive (forbidden) as infrared and Raman transitions from the ground state. The individual lines in the infrared spectra observed in the present work under high resolution exhibit an alternation in their intensities that illustrate nicely the role of nuclear spin statistics derived from the equivalent, symmetrically-positioned atoms. For the propellane molecule with isotopic composition $^{12}C_5H_6$, the nuclear spin statistical weights for a totally symmetric vibronic state are 24 for *K* mod(3) = 0 and are 20 otherwise, except for *K* = 0 where the weight is 16 for *J* odd and 8 for *J* even. These weights are the same, irrespective of whether the methylene groups lie in the σ_h plane, as shown in Fig. 1 or stand perpendicular or obliquely to it (D_3 configuration); *ab initio* and experimental evidence favors the D_{3h} arrangement.

2. Experimental details and results

Propellane was synthesized as described earlier [1,2] using the methods described in Ref. [9]. Infrared spectra in the ν_9 region were taken at an instrumental resolution of 0.0025 cm^{-1} using a Bruker IFS 120 FTIR spectrometer located at the Pacific Northwest National Laboratory[1]. The sample pressure was 63 Pa (0.47 torr) and the multiple-reflection White cell employed was adjusted for an optical path length of 25.6 m. The spectrometer was evacuated and equipped with a Globar light source and an MCT detector. Boxcar apodization was used and 640 single-sided interferograms were collected with both forward and backward scans. For the far infrared study of the $\nu_4 - \nu_{15}$ (A_2'') parallel band, a Bruker 120 instrument equipped with a bolometer detector was employed and the resolution was 0.0020 cm^{-1}. The sample pressure was 330 Pa (2.5 torr), the path length was 28.8 m, and the number of scans collected was 256. The spectrometers were calibrated with N_2O and H_2O lines and the absolute wavenumber values are believed to be accurate to about 0.00015 cm^{-1}.

Fig. 2 shows an overview, from 1400 to 1550 cm^{-1}, of the observed spectrum that makes up the region of the ν_9 band. Also shown are simulated spectra of the four assigned bands to illustrate the degree of congestion and overlap with the strong ν_9 band. The inset on the upper right hand side shows the two normal mode components of the doubly degenerate ν_9 vibration, which is principally a hydrogen-bending mode. The view is along the C_3 axis so the axial carbons are not distinguished.

3. Band analysis and discussion

3.1. Rovibrational level expressions

Propellane is an oblate symmetric top molecule with principal moments of inertia $I_B < I_C$. The rotation constants are then given as $B > C$ in which $B = h/(8\pi^2 cI_B)$ and likewise for *C*, where *h* is Planck's constant and *c* is the speed of light in vacuum. The physical constants are chosen such that the rotational constants are expressed in units of cm^{-1}.

The energy of a given vibrational state, v, is given by

$$E_v = G(v, l) + F_v(J, K, l) \quad (1)$$

where $G(v, l)$ is the vibrational term, and $F_v(J, K, l)$ is the rotational term which may be divided into two parts

$$F_v(J, K, l) = F_v(J, K) + F_{v_\perp}(J, k, l). \quad (2)$$

For the present work when only non-degenerate vibrational modes are involved $F_v(J, K, l)$ is given solely by

$$\begin{aligned} F_v(J,K) = {} & B_v J(J+1) + (C_v - B_v)K^2 \\ & - D_v^J J^2(J+1)^2 - D_v^{JK} J(J+1)K^2 - D_v^K K^4 \\ & + H_v^J J^3(J+1)^3 + H_v^{JK} J^2(J+1)^2 K^2 + H_v^{KJ} J(J+1)K^4 + H_v^K K^6 \\ & \pm \delta_{3K}\Delta_3 J(J+1)[J(J+1)-2][J(J+1)-6] + \ldots \end{aligned} \quad (3)$$

Here the last term corresponds to the splitting of the $K = 3$, $l = 0$ levels into an A_1, A_2 pair. For doubly degenerate vibrational states, the $K = 3$ splitting term is omitted and the rotational term expression requires the second term

$$\begin{aligned} F_{v\perp}(J,k,l) = {} & -2(C\zeta)_v kl + \eta_v^J J(J+1)kl + \eta_v^K k^3 l \\ & + \eta_v^{JJ} J^2(J+1)^2 kl + \eta_v^{JK} J(J+1)k^3 l + \eta_v^{KK} k^5 l \\ & \pm \delta_{-1l}\delta_{2k} t_v [J(J+1)][J(J+1)-2]. \end{aligned} \quad (4)$$

The last term in Eq. (4) accounts for the splitting of the $kl = -2$ levels into an A_1, A_2 pair. For even *J* the upper sign applies to the A_1 level and the lower sign applies to the A_2 level and for odd *J* the reverse applies.

In these expressions *J* is the total angular momentum quantum number, *K* is the projection of *J* onto the principal C_3 symmetry axis, *k* is the signed projection of *J* onto the symmetry axis, so that $K = |k|$, and *l* is the vibrational angular momentum quantum number. The $(C\zeta)_v$ term in Eq. (4) accounts for the intra-vibrational Coriolis interactions; when the product $(C\zeta)_v$ *kl* is positive (negative) the vibrational and rotational angular momenta combine to give a lower (higher) energy. The contracted subscript *v* is used to represent both quantum number and mode number of a vibrational state. For the ground state $v_1 = v_2 = v_3 = \ldots = 0$. The zero energy is defined as the $J = K = 0$ level of the ground state, *i.e.*, $\nu_0 = G(v, l) - G(0, 0)$.

For both the $K = 2$ and $K = 3$ splittings the A_1, A_2 level order is sometimes dictated by the inclusion of certain off-diagonal matrix elements that mix in other states. Because of that, the signs of the splitting constants are not an infallible clue to whether the A_1 level

[1] Certain commercial equipment, instruments, and materials are identified in the paper to adequately specify the experimental procedure. Such identification does not imply recommendations or endorsements by the National Institute of Standards and Technology or the Pacific Northwest National Laboratory, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.