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## Vibration-Rotational Bands of Butadiene-1,3: Evidence for Coriolis Coupling

Four bands,  $\nu_{10}$  at 1013.2,  $\nu_{11}$  at 907.8,  $\nu_{12}$  at 524.5, and  $\nu_{22}$  at 1296.2 cm<sup>-1</sup> have had analysis of their K-structure to yield a new value of the ground state rotational constant,  $(A'' - \bar{B}'') = 1.251 \pm 0.004$  cm<sup>-1</sup>. Coriolis coupling is discovered between  $\nu_{23}$  at 990.6 cm<sup>-1</sup> and each of  $\nu_{10}$  and  $\nu_{11}$ . The coupling constant  $|\xi_{11,23}^{z}|$  has a magnitude 0.46  $\pm$  0.03.

We have measured some vibration-rotational bands of butadiene-1,3- $h_6$  vapor in absorption. Phillips 66 research grade gas was used; carbon monoxide, the only detectable impurity, was removed by pumping on the solid condensed at liquid nitrogen temperature. Spectra were recorded on a Perkin-Elmer 225 spectrometer with the sample enclosed in a 100-mm cell with KBr windows. The spectrometer was calibrated with standard absorption lines of water, carbon dioxide, ammonia, and hydrogen and deuterium cyanide vapors. Sample temperature in the spectrometer was about 320°K.

Several bands showed resolvable fine structure under the conditions of measurement (spectral slit widths 0.2–0.7 cm<sup>-1</sup>). Quantum numbers were assigned in the prolate symmetric rotor approximation which is satisfactory as Ray's asymmetry parameter  $\kappa = -0.98$  ( $\kappa = -1.0$  in the prolate symmetric rotor limit). The K-structure of bands was analyzed using the following combination sum and difference formulas (1):

$${}^{R}Q_{K} + {}^{P}Q_{K} = 2[\nu_{0} + (A' - B')] + 2[(A' - B') - (A'' - B'')]K^{2};$$
  

$${}^{R}Q_{K} - {}^{P}Q_{K} = 4(A' - \bar{B}')K;$$
  

$$Q_{K-1} - {}^{P}Q_{K+1} = 4(A'' - \bar{B}'')K,$$

in the usual notation. Data were subjected to a full statistical analysis with machine-run least squares programmes.

We present results for four bands. Illustrated in Fig. 1a, a type-B band near 1300 cm<sup>-1</sup>, designated  $\nu_{22}$ , is due to an inplane C-II bending vibration  $(B_u \text{ symmetry species})$ . Rotational analysis yielded the results:  $\nu_0 = 1296.23 \pm 0.06$ ;  $(A'' - \bar{B}'') = 1.258 \pm 0.003$ ;  $(A' - \bar{B}') = 1.255 \pm 0.003$ ;  $(A' - \bar{B}') - (A'' - \bar{B}'') = -0.0015 \pm 0.0002 \text{ cm}^{-1}$ . Shown in Fig. 1b, a type-C band with a prominent central branch near 1013 cm<sup>-1</sup>,  $\nu_{10}$ , is due to an out-of-plane methylene twisting vibration. Analysis of the complicated structure gave:  $\nu_0 = 1013.2 \pm 0.2$ ;  $(A'' - \bar{B}'') = 1.212 \pm 0.02$ ;  $(A' - \bar{B}') = 1.220 \pm 0.015$ ;  $(A' - \bar{B}') - (A'' - \bar{B}'') = +0.0105 \pm 0.0015 \text{ cm}^{-1}$ . Another type-C band,  $\nu_{11}$ , arises from the methylene wagging fundamental mode  $(A_u)$ :  $\nu_0 = 907.78 \pm 0.03$ ;  $(A'' - \bar{B}'') = 1.251 \pm 0.002$ ;  $(A' - \bar{B}') = 1.235 \pm 0.002$ ;  $(A' - \bar{B}') - (A'' - \bar{B}'') = -0.0202 \pm 0.00014 \text{ cm}^{-1}$ . A third type-C band,  $\nu_{12}$ , arises from an out-of-plane skeletal wagging motion  $(A_u)$ :  $\nu_0 = 524.5 \pm 0.1$ ;  $(A'' - \bar{B}'') = 1.245 \pm 0.0015$ ;  $(A' - \bar{B}'') = -0.0022 \pm 0.00014 \text{ cm}^{-1}$ .

All bands which have fine structure show more than one series of  ${}^{P}Q$ - and  ${}^{R}Q$ -lines because of hot bands. Three hot bands have already been measured (2) in connection with the most intense fundamental,  $\nu_{11}$  at 908 cm<sup>-1</sup>. These superimposed hot bands cause inaccuracy in measurement of wavenumbers of lines for the fundamental bands presented





FIG. 1. Infrared absorption between (a) 1430-1210; (b) 1090-980 cm<sup>-1</sup> of butadiene vapor at pressures (a) 200; (b) 40 hN m<sup>-2</sup> in 100-mm path. Spectral slit width is 0.20-0.26 cm<sup>-1</sup>.

above. Another cause of inaccuracy is the slightly nonlinear scan of the spectrometer, for which correction from calibration lines is not quite adequate. These two effects, mostly the first, produced rather poor agreement in the effective ground state rotational constants for the different vibrations, such that discrepancies exceed the nominal standard deviations. A weighted mean of the quantity  $(A'' - \bar{B}'')$  for the  $\nu_{11}$ ,  $\nu_{12}$ , and  $\nu_{22}$  fundamentals is  $1.251 \pm 0.004$  cm<sup>-1</sup>. (The result for  $\nu_{10}$  was excluded entirely because of large standard deviation caused by band overlapping and few measurable lines.) That mean is not significantly different from the single value for  $\nu_{11}$  previously published (2),  $1.246 \pm 0.002$  cm<sup>-1</sup>. Other values obtained under much poorer resolution are  $1.23 \pm 0.01$  (3) for  $\nu_{11}$  also, and 1.21 cm<sup>-1</sup> (4) for  $\nu_{13}$ .

More interesting are the relatively large values of  $(A' - \bar{B}') - (A'' - \bar{B}'')$  for the 907.8  $cm^{-1}$  band,  $\nu_{11}$ , and the 1013  $cm^{-1}$  band,  $\nu_{10}$ , in comparison with those of  $\nu_{12}$  and  $\nu_{22}$ . Although the value for  $\nu_{10}$  is probably somewhat unreliable at the nominal stated accuracy, we have much greater confidence in the value for  $\nu_{11}$ , which in fact agrees well with the previous accurate determination (2),  $-0.0200 \pm 0.0003$  cm<sup>-1</sup>. We propose that these large apparent  $\alpha$ -values in fact reflect the occurrence of a Coriolis interaction between each of  $\nu_{10}$  and  $\nu_{11}$  with a third fundamental mode. According to Jahn's rule, Coriolis coupling will occur between two vibrational modes if the direct product of their symmetry species transforms like a molecular rotation. When a  $B_u$  vibration has a transition moment almost parallel to the intermediate inertial axis, detection becomes particularly favorable, as interaction with the  $A_{\mu}$  vibrations of moment necessarily parallel to the major inertial axis gives rise to Coriolis forces about the least inertial axis (5). Therefore effects become observable in the spacing of the  $\Delta J = 0$ ,  $\Delta K = \pm 1$  transitions which can be resolved. Large  $\alpha$ -values, of opposite signs, appear for the A rotational constants of interacting bands, but really the Coriolis effect accounts for 75-90% of the magnitude of  $\alpha$ . Intensities of various branches are also affected.

NOTES

In the particular case of butadiene-1,3, this  $\alpha$ -value effect is readily detected. For  $\nu_{11}$ ,  $(A' - \bar{B}') - (A'' - \bar{B}'') = -0.0202$ , whereas for  $\nu_{10}$ , this quantity equals +0.010. This situation is compatible with both vibrations interacting separately through Coriolis coupling with a  $B_u$  vibration of wavenumber between 908 and 1013 cm<sup>-1</sup>. Coriolis coupling is appreciable only if the interacting bands are of similar wavenumber. Visible in Fig. 1b, the type-B band with a central minimum at 990.6 cm<sup>-1</sup> fulfills all the requirements; it is designated  $\nu_{23}$ , a methylene rocking mode with transition moment almost parallel with the intermediate inertial axis. Unfortunately no K-structure of this band could be clearly distinguished to prove the participation. An estimate of the Coriolis coefficient can be obtained from second-order perturbation theory (6). The second-order correction to the rotational levels of  $\nu_{11} = 1$  is  $-4A^2\xi_{11,23}^{2}K^2/(\nu_{23} - \nu_{11})$ . With  $\nu_{23} = 990.6$ ,  $\nu_{11} = 907.8$ ,  $(A - \bar{B}) = 1.251$ ,  $\bar{B} = 0.1413$  (3), so that A = 1.392 cm<sup>-1</sup>, and assuming all of the magnitude of  $\alpha$  is due to the Coriolis interaction, we can insert these numbers into the expression

$$\alpha = -4A^{2}\zeta_{11,23}^{2}/(\nu_{23}-\nu_{11})$$

to obtain  $|\xi_{11,23}^i| = 0.46 \pm 0.03$ . Similarly an estimate of  $|\xi_{10,23}^i|$  can be made, but the result, 0.17, is much less significant because of the inaccuracy of the rotational constants. (If only 80% of the magnitude of  $\alpha$  in each case were due to Coriolis interaction, then the values of  $\zeta$  would be 0.41 and 0.15, respectively.) For comparison with 0.46, other molecules with analogous couplings involving methylene groups have  $\zeta$ -values as follows: ethene (6), 0.44  $\pm$  0.02; propadiene (7), 0.53 and 0.56; and methanal (H<sub>2</sub>CO) (8), 0.54.

In methanal azine,  $H_2C=N-N=CH_2$ , proved (9) to have an s-transoid conformation like butadiene-1,3, the effects on the  $\alpha$ -values for both the type-B and type-C bands are detected, as well as intensity effects. In this case, the derived value of  $|\zeta_{s,17}^{z}| = 0.49 \pm 0.05$ .

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