THE QUASILINEAR NATURE OF SOME SIMPLE COVALENT FULMINATES XCNO, AS REVEALED BY ROTATIONAL SPECTROSCOPY IN THE MMW RANGE

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The rotational spectra of the unstable molecules BrCNO, ClCNO, and NCCNO have been recorded at room temperature using three backward wave oscillators that cover the spectral range from 52 to 179 GHz. In addition, the frequency range between 210 and 230 GHz has been investigated by means of a frequency doubler. All measurements have been carried out at a pressure of approx. 1 Pa in a flow system, the sample molecule being synthesized directly at the inlet of a free space absorption cell by gas phase pyrolysis of a volatile precursor.

The a-type spectra of the halofulminates BrCNO and ClCNO both are characterized by a large number of intense satellite lines. The patterns formed by the satellites for the two molecules are found to be very similar to each other, but clearly different from both the (v_t, l_t) satellite pattern of a regular linear molecule and the (v_b, K_a) satellite pattern of a regular near prolate asymmetric top. This indicates very anharmonic XCN bending potentials resulting in extremely quasilinear XCN bending modes, definitely more quasilinear than the HCN bending mode in HCNO[a]. Compared to the CCC bending mode in OCCCO, so far the most quasilinear molecule known, the XCN bending modes in BrCNO and ClCNO appear to be slightly closer to the bent limiting case.

The rotational spectrum of NCCNO, on the other hand, exhibits only moderate deviations from the spectrum of a regular linear molecule, clearly smaller than those found for HCNO. Altogether, our results suggest that π-electron donating substituents X give rise to more bent XCNO molecules, whereas π-electron withdrawing substituents X result in more linear XCNO molecules.

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