HIGH-RESOLUTION LASER PHOTOACOUSTIC SPECTROSCOPY OF PH_3 : THE FIFTH P-H STRETCHING OVERTONE BANDS.

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A titanium:sapphire ring laser (Coherent 899-29) pumped by an Innova 400, 15 W argon-ion laser was coupled to a high sensitivity acoustic cell (α_{min} = 5x10^{-9} cm^{-1}) filled with PH_3. The cell is an acoustic resonator built from stainless steel pipe (10 cm length, i.d. 6 mm) and equipped with two buffer volumes of 5 cm at both ends in order to reduce the ambient noise. The laser beam was chopped at 1370 Hz for exciting the first longitudinal mode of the resonator. The photoacoustic signal was detected by two electret microphones (Knowles EK-3024) mounted on a summing amplifier circuit and converted to a DC voltage by a lock -in-amplifier. Most spectra were recorded with a laser power of 1.5 W and using a time constant of 300 ms, with a typical sensitivity of 100-500 μV. The spectrum of phosphine has been recorded at room temperature with a gas pressure of 116 hPa between 12 500 and 12 780 cm^{-1}.
The Δv=6 spectrum is characterized by one band system centered at 12 678 cm^{-1}. It is assigned to the local mode P-H stretching (600 A_1/E) bands. The analysis started by locating the most intense ^rR_K(J) and ^pP_K(J) lines (with K=J) and the $^rQ_0$(J) lines of the perpendicular band, using the ground state combination differences technique. Forty-four lines associated with J, K = 0-9, 0-9 have been assigned up to now. For the weak parallel band, only 11 lines up to J=4 have been assigned. The lines have been fitted with a Hamiltonian model which makes use of simple arithmetic relations between some rovibrational parameters (H. Buerger, M. Lecoutre, T.R. Huet, J. Breidung, W. Thiel, V. Hanninen and L. Halonen, *J. Chem. Phys.* 114 (2001) 8844, and Ref. therein). The program written by L. Halonen was used (L. Halonen, private communication). The ground state constants were kept fixed to the values from the litterature (L. Fusina and G. Di Lonardo, *J. Mol. Struct.* 517-518 (2000) 67-78). No perturbation was observed at this stage of the analysis. The molecular parameters seem to confirm the local mode tendency of the PH_3 molecule in the near infrared range.
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