THE NEAR IR BULK and JET-COOLED NO_2 SPECTRA by FTS, ICLAS, CRDS and LIF

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In order to characterize experimentally the $\widetilde{X}\,^2A_1 - \widetilde{A}\,^2B_2$ conical intersection in $\mathrm{NO_2}$ we have extensively studied its near IR spectrum, both in a bulk cell and in a slit jet expansion. The advantages and disadvantages of the four techniques (FTS, ICLAS, CRDS, LIF) will be briefly summarized and there performances compared. Actually, only the slit jet spectra are analyzable, the room temperature spectrum being highly congested. More than 100 vibronic levels belonging to the $^2B_2$ symmetry have been observed by absorption from 10800 to 13900 cm^{-1} whereas only 15 vibrational levels of the $\widetilde{A}\,^2B_2$ state (bright levels) are expected in that range. The $\widetilde{X}\,^2A_1 - \widetilde{A}\,^2B_2$ vibronic interactions strongly mix the (dark) set of $\widetilde{X}\,^2A_1$ levels (about 85 levels belonging to the $^2B_2$ symmetry) with the set of 15 $\widetilde{A}\,^2B_2$ bright levels. In addition, numerous hot bands have also been observed in that range. Most of these vibronic levels have an irregular rotational structure, even if most of the K-subbands seem almost regular. This results from the combination of large energy differences between interacting levels and large matrix elements leading to smoothly varying mixing coefficients in each K stack. The iterative comparison of the band origins, intensities and rotational constants with those predicted by a model Hamiltonian is the clue of the understanding of the $\mathrm{NO_2}$ conical intersection.