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Comparison of the photodissociation dynamics of alkyl nitrites in the A and B absorption bands

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Alkyl nitrites (R−ONO, R=CH_3, *n*-C_3H_7, *t*-C4H9) have been widely studied due to the efficient photodissociation and formation of NO fragment.[1,2] The absorption spectra of all these molecules present two bands. A first band characterized by a clear vibronic structure, and a second more intense band which extends to the VUV energy reagion.[2,3] In this work, three different alkyl nitrites where studied, CH_3ONO, *n*-C_3H_7ONO, and *t*-C_4H_9ONO, so a comparison of the hydrocarbon chain on the photodissociation dynamics could be made.[4] The study was performed in the two absorption bands (A and B) independently. Pump-probe experiments using nanosecond laser pulses in combination with velocity map imaging detection of NO by $(1 + 1)$ REMPI were carried out.

The results in the A band show a shift in the kinetic energy distributions as higher vibrational states for a fixed rotational quantum number $J = 19.5$ of the NO fragments were detected. By comparing the three molecules, a larger shift in energy is also present, a displacement previously observed in the studies of alkyl halogen molecules.[4] Several differences in the shape of the kinetic energy distributions, and in the angular distributions, were also detected. Meanwhile, the B band show a parallel transition in contrast to the perpendicular transitions observed in the A band. In this case, several contributions could be observed for each of the measurements performed.

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