PHOTO-DISSOCIATION RESONANCES OF JET-COOLED NO_2 AT THE DISSOCIATION THRESHOLD BY CW-CRDS, CHALLENGING RRKM THEORIES

PATRICK DUPRÉ, *Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, Dunkerque, France*.

Around 398 nm, the jet-cooled NO_2 spectrum exhibits a well identified dissociation threshold (D_0). Combining LIF detection and continuous-wave absorption-based CRDS technique a frequency range of $\sim 25\,\mathrm{cm}^{-1}$ is analyzed at high resolution around D_0. In addition to the usual rovibronic transitions towards long-lived energy levels, ~ 115 wider resonances are observed. Over this energy range, the resonance widths spread from $\sim 0.006\,\mathrm{cm}^{-1}$ ($\sim 450\,\mathrm{ps}$) to $\sim 0.7\,\mathrm{cm}^{-1}$ ($\sim 4\,\mathrm{ps}$) with large fluctuations. At least two ranges of resonance width can be identified when increasing the excess energy. They are associated with the opening of the dissociation channels $NO_2 \rightarrow NO\left(X\,^2\Pi_{1/2},\, v=0,\, J=1/2\right) + O\left(^3P_2\right)$ and $NO_2 \rightarrow NO\left(X\,^2\Pi_{1/2},\, v=0,\, J=3/2\right) + O\left(^3P_2\right)$. Weighted mean unimolecular dissociation rate coefficients k_{uni} are calculated. The density of reactants (following the RRKM predictions) is deduced, and it will be discussed versus the density of transitions, the density of resonances and the density of vibronic levels. The data are analyzed in the light of time-resolved data previously reported. This analysis corroborates the existence of loose transition states along the reaction path close to the dissociation energy in agreement with the phase space theory predictions[a].

[a] [Accpeted in J. Chem. Phys.]