Photo-dissociation Resonances of Jet-Cooled NO_2 at the Dissociation Threshold by CW-CRDS

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Abstract

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 transitions exciting long-lived energy levels, $\sim$ 115 wider resonances are observed. The resonance widths spread from $\sim 0.006\,\mathrm{cm}^{-1}$ (450 ps) to $\sim 0.7\,\mathrm{cm}^{-1}$ (4 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 $NO_2 \rightarrow NO\left(X^2\Pi_{1/2}, v=0, J=3/2\right) + O\left(^3P_2\right)$. This analysis corroborates the existence of loose transition states along the dissociation coordinate close to the dissociation energy in agreement with the phase space theory predictions. The data are analyzed in the light of previously reported frequency- and time-resolved data to provide a robust determination of mean unimolecular dissociation rate coefficients k_{uni}. The density of reactant levels deduced will be discussed versus the density of transitions, the density of resonances and the density of vibronic levels.

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