VIBRONIC INTERACTION AND VIBRATIONAL ASSIGNMENT FOR NO$_3$ IN THE GROUND ELECTRONIC STATE

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The strongest IR band of NO$_3$ appears at 1492 cm$^{-1}$ and has been assigned traditionally to the N-O degenerate stretching $\nu_3$ mode. In 2007 Stanton proposed the $\nu_3$ to be about 500 cm$^{-1}$ lower, i.e. it is located around 1000 cm$^{-1}$, based on theoretical calculations. Jacox and collaborators supported this proposal, on the basis of their IR spectra observed in Ne matrix, and reassigned the 1492 cm$^{-1}$ band to $\nu_3 + \nu_4$. The traditional vibrational assignment is referred to as Assignment I and the Stanton-Jacox one as Assignment II, and thus the upper state of the 1492 cm$^{-1}$ band Z is $\nu_3$ and $\nu_3 + \nu_4$ for Assignment I and II, respectively.

Kawaguchi, Ishiwata, and Hirota (KIH) have been making much effort to settle which assignment is correct, by observing and analyzing FTIR spectra. They thought in 2009 that the observation of hot bands from the in-plane ONO degenerate bending $\nu_4$ state to the Z state will make it possible for KIH to select the correct assignment among the two. Namely for Assignment I only one hot band of E - E type (i.e. $\nu_3 - \nu_4$) will appear, whereas three bands for Assignment II: E - E, A$_1$ - E, and A$_2$ - E. It was straightforward to detect and assign the E - E type hot band, because the upper state is Z in common with that of the 1492 cm$^{-1}$ band. After careful searching for the spectra, KIH arrived at a conclusion that there is only one A - E type hot band present, which is difficult to reconcile with Assignment II, and the observed A - E hot band is reasonably ascribed to $2\nu_2 - \nu_4$ in Assignment I.

The NO$_3$ radical has been thought to be subjected to strong vibronic interaction. This view originated from an anomalous $\nu_4$ progression appearing in the NO$_3^-$ photoelectron spectra by Neumark et al.; they explained this observation in terms of Herzberg-Teller (H-T) effect with a sizable interaction parameter. However, KIH did not observe any anomalous features in the $\nu_4$ vibration-rotation structure, which would be caused by the huge H-T perturbation as presumed by Neumark. Hirota found that the $\nu_4$ progression of Neumark can be explained by the coupling of the unpaired electron orbital angular momentum with that of the $\nu_4$ mode in the ground electronic state.