

Collisional quenching of excited NO ($A^2\Sigma^+$) studied by time-resolved FTIR emission spectroscopy

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Time-resolved FTIR emission spectroscopy has been used to determine the fate of electronically excited NO following collisions with a number of quenching species. Quenching of NO ($A^2\Sigma^+$ $\nu=0$) by atomic xenon results in emission from NO ($X^2\Pi$, $\nu=1-22$), but yields a vibrational distribution unlike that seen following quenching by any other rare gas atom (see figure 1). In stark contrast to the vibrational distributions observed following quenching of electronically excited NO by He, Ne, Ar and Kr, quenching by Xe produces a far greater fraction of vibrationally excited NO in the ground state. Given that Xe is a slow quencher of NO ($A^2\Sigma$ $\nu=0$), these populations cannot be produced by direct collisional quenching of the $A^2\Sigma^+$ state. A series of experiments observing the IR emission from NO ($X^2\Pi$) in different conditions provide evidence of an alternative process involving the formation of NO ($a^4\Pi$) which we predict will produce vibrationally excited NO.

IR emission from within NO ($X^2\Pi$) has also been observed following self-quenching of NO ($A^2\Sigma$ $\nu=1$). The nascent vibrational distribution of ground state NO was found to be largely similar to the equivalent self-quenching of NO ($A^2\Sigma^+$ $\nu=0$), with additional emission from the excited A state molecule and vibrationally excited N₂O. With O₂ as the quencher, both reactive and non-reactive quenching are observed. The behaviour of these quenchers is discussed for the $\nu=1$ state of NO $A^2\Sigma^+$, and quenching dynamics are compared and contrasted with the previously studied $\nu=0$ systems.

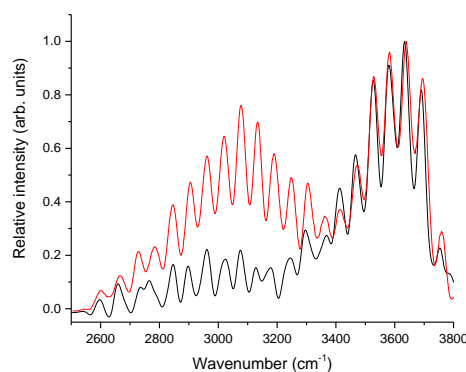


Figure 1: The infrared emission resulting from overtone transitions ($\Delta\nu = -2$) within NO $X^2\Pi$ observed at 5 μs following irradiation of 50 mTorr NO, to form NO $A^2\Sigma^+$ ($\nu = 0$), in the presence of 600 Torr Xe (red line). For comparison, the emission spectrum observed in the presence of 500 Torr Ar (black line) is also included.