UNEXPECTED DOPPLER SHIFTS FROM A NEUTRAL MOLECULE IN AN ELECTRICAL DISCHARGE DETECTED BY VELOCITY MODULATION FTS.

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Velocity-modulation Fourier transform [a] emission spectra from an $N_2O$/He discharge plasma recorded between 1 800 and 10 000 $cm^{-1}$ are described. Surprisingly, they show Doppler shifted lines of the $E\,^2\Sigma^+$-$D\,^2\Sigma^+$ , $C\,^2\Pi$-$A\,^2\Sigma^+$, and $D\,^2\Sigma^+$-$A\,^2\Sigma^+$ Rydberg-Rydberg rovibronic transitions of the nitric oxide neutral molecule. $N_2$ transitions, with comparable intensities are also present in the spectra and remain unshifted.

Mostly in laser spectroscopy, velocity modulation [b] has been since 1983 a successful technique developed for the search and characterization of molecular ions. Doppler shifts in transition frequencies of ions, which result from the drift velocities in the electric field of plasma, provide selective detection. Doppler shifted neutral species have been scarcely reported. To our knowledge the only interpretations of such observations were given for $H_2$ [c] and for He [d]. Both behaved like anions and the origin of their shifts was identified as deriving from momentum transfer in electron-molecule collisions.

This is not the case in the present experiments where NO acts like a positively charged particle. Experimental investigations and tentative explanations of these observations are discussed.

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