

Synchrotron radiation study of the vacuum UV photodissociation of some NO-containing compounds

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Fluorescence from electronically excited NO resulting from the photodissociation of organic nitrites (CH_3ONO , CD_3ONO , $\text{C}_2\text{H}_5\text{ONO}$ and $(\text{CH}_3)_2\text{CHONO}$) and ClNO was investigated using synchrotron radiation from the Orsay Electron Storage Ring as the source of excitation in the 1200 - 1700 Å region. The production of the NO states A $^2\Sigma^+$, C $^2\Pi$ and D $^2\Sigma^+$ was evidenced from energy- and time-resolved spectra; the fluorescence excitation spectra of individual electronic states are reported and compared with the absorption spectra of the parent molecule. The vibrational energy distribution in the NO A state was determined as a function of incident wavelength. The results are discussed in terms of a statistical energy partitioning and show a contrast in behaviour between the triatomic ClNO molecule and the polyatomic nitrites.

On the validity of several methods of calculation of vibronic energy relaxation rates

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Various approximation methods of calculating the rates of vibronic energy relaxation are studied and compared with an exact (numerical) method. The molecular vibrations are described by harmonic oscillators, the positions of equilibrium of which are assumed to be different in different electronic states. The finite linewidths of the vibronic states are taken into account. It is found that the approximation methods (such as the method of steepest descent) provide values of the relaxation rates that are too small, particularly as the coupling strength becomes weak. The effect of anharmonic molecular vibrations is briefly discussed.