STUDIES OF NO₂ BY LIF AND BOLOMETRIC DETECTION


The vibrational structure of the visible absorption spectrum of NO₂ is dominated by a strong conical intersection between the potential energy surfaces of the electronic ground state $\tilde{X} \tilde{A}_1$ and of the first electronically excited state $\tilde{A} \tilde{B}_2$, which occurs around 10,000 cm⁻¹. Above the conical intersection the vibronic levels can be built of $\tilde{A}_1$ vibrational levels in the $\tilde{B}_2$ electronic state as well as the coupled high $\tilde{B}_2$ vibrational levels in the $\tilde{A}_1$ electronic ground state, forming so-called hybrid states. This explains the dense spectra with many more lines than expected on the basis of the first electronically excited state only, causing an apparently chaotic frequency distribution of these hybrid states.

To unravel the behaviour of the hybrid states, we measured the hyperfine structure. The main contribution to the hyperfine interaction is the Fermi-contact interaction, which is about 150 MHz for the electronic ground state and almost zero for the first electronically excited (diabatic) state. So the magnitude of the hyperfine constant of the hybrid excited state provides information about the contribution of the high vibrational levels of the electronic ground state in the excited hybrid state.

In our laboratory we excite a supersonically cooled beam of NO₂ molecules with a Ti:Sapphire ring laser in the energy range of 11210 - 13680 cm⁻¹. The molecular beam is detected using a bolometer. In addition, the fluorescence is detected using a photomultiplier. By this we get information of the energy region just above the conical intersection, the region were the vibronic chaos will start taking place.

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