PROGRESS IN THE UNDERSTANDING OF THE NEAR-IR SPECTRUM OF $^2\Sigma$ AND $^2\Pi$ CCBr

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Near infrared spectra of a linear radical tentatively identified as CCBr were first detected during the ultraviolet laser photolysis of bromoform and reported by us at the 55th Symposium.[b] Several P-branch structures were observed near 9550 cm^{-1} and 11230 cm^{-1} but at the time no detailed assignments were possible. These data remain the only reported experimental observation of the radical, which is expected to possess three low-lying doublet electronic states, derived from $^2\Sigma$ and $^2\Pi$ states at linearity. There has recently been renewed theoretical interest in this and similar triatomic systems possessing multiple, closely-spaced, electronic surfaces all of which are involved in vibronic interactions that cause a breakdown of the Born-Oppenheimer approximation. In the case of CCBr, the $^2\Sigma$ and $^2\Pi$ states are separated by less than 500 cm^{-1} [c]. The computed vibronic absorption spectrum in the infrared and near-infrared is both extensive and irregular. However by making use of the results of Tarroni and Carter,[c] we have been able to make considerable progress in understanding the structure of the observed spectra and making rotational assignments. Further analysis and the results of new experimental efforts to record spectra under jet-cooled conditions will be reported.

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[b]N. Hansen, A. J. Marr and T. J. Sears, Paper TA06, 55th International Symposium on Molecular Spectroscopy, Columbus Ohio, 12-16 June, 2000

[c]R. Tarroni and S. Carter, Mol. Phys. **104**, 2821-2828 (2006); S. Mishra, V. Vallet, L. Poluyanov and W. Domcke, J. Chem. Phys. **125**, 164327, (2006)