FLUORESCENCE EXCITATION SPECTROSCOPY AND LIFETIMES OF THE A\(^1\)B\(_1\)-X\(^1\)A\(_1\) SYSTEM OF CCl\(_2\)

C. TAO, M. DESELNICU, C. MUKARAKATE AND S. A. REID, Department of Chemistry, Marquette University, Milwaukee, WI 53201-1881; T. W. SCHMIDT AND S. H. KABLE, School of Chemistry, University of Sydney, NSW 2006, Australia.

We report a comprehensive new study of the electronic spectroscopy of the A\(^1\)B\(_1\)-X\(^1\)A\(_1\) system of CCl\(_2\) in the region 400-600 nm. The spectra were measured under jet-cooled conditions using a pulsed discharge source, and rotationally analyzed to yield precise values for the band origins and \(A\) rotational constants. As described by Kable and co-workers,\(^a\) the spectrum can be separated into three distinct regions. Region 1, lying below 20300 cm\(^{-1}\), displays regular vibrational structure, and a Dunham expansion fit of the band origins for the C\(^35\)Cl\(_2\) and C\(^35\)Cl\(^37\)Cl isotopomers reproduces the experimental term energies to within a standard deviation of < 1 cm\(^{-1}\). In region 2, lying between 20300 cm\(^{-1}\) and roughly 21500 cm\(^{-1}\), the rotational structure of the bands is largely unperturbed; however, vibrational mixing is extensive due to near resonances among the states \(1^a\)\(^2\)\(_m\) having the same polyad number \(\nu = 2r + m\). Above 21500 cm\(^{-1}\) (Region 3), the rotational structure of the bands changes markedly, such that above 22500 cm\(^{-1}\) only subbands terminating in \(K^\prime_a = 0\) appear strongly in the spectra, indicating that the Renner-Teller (RT) intersection has been exceeded. In this talk, we will focus on the correlation of spectra and lifetime measurements; as found for other simple carbenes, the approach to the RT intersection is evidenced in a pronounced lifetime lengthening for states with \(K^\prime_a > 0\). The measured \(A\) rotational constants exhibit a sudden and significant increase in the vicinity of the barrier. We will also compare our lifetime measurements with previous experimental results. Good agreement is found with a previous matrix isolation study when accounting for matrix effects; however, our lifetimes are not in good agreement with most previous gas-phase studies.