FLUORESCENCE EXCITATION SPECTROSCOPY AND LIFETIMES OF THE A^1B_1-X^1A_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^1B_1-X^1A_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^n2^m having the same polyad number p=2n+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 $K'_a = 0$ 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 $K'_a > 0$. 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.

[a] J. S. Guss, et al., Phys. Chem. Chem. Phys. 7, 100 (2005).