EFFECTS OF A REMOTE BINDING PARTNER ON THE ELECTRIC FIELD AND ELECTRIC FIELD GRADIENT AT AN ATOM IN A WEAKLY BOUND TRIMER: MICROWAVE SPECTROSCOPY AND QUANTUM MECHANICAL COMPUTATIONS ON Kr-SO_3 AND Kr-SO_3-CO

REBECCA B. MACKENZIE, BROOKE A. TIMP, KENNETH R. LEOPOLD, *Department of Chemistry, University of Minnesota, 207 Pleasant St., SE, Minneapolis, MN 55455*; YIRONG MO, *Department of Chemistry, Western Michigan University, Kalamazoo, MI 49008*.

Microwave spectra have been recorded for the C_{3v} symmetric complexes Kr-SO_3 and Kr-SO_3-CO. The Kr-S distances are 3.438(3) Å in Kr-SO_3 and 3.488(6) Å in Kr-SO_3-CO. Thus, the addition of CO to Kr-SO_3 increases the Kr-S distance by 0.050(9) Å. In contrast, the C-S distance in the trimer, 2.871(9) Å, is the same as that previously determined for SO_3-CO to within the estimated uncertainties. Observed values of the ^{83}Kr nuclear quadrupole coupling constants provide direct probes of the electric field gradient at the Kr nucleus. We find that, although the Kr and CO in the trimer are on opposite sides of the SO_3 and are thus not in direct contact, the addition of CO to Kr-SO_3 reduces the electric field gradient at the Kr nucleus by 18%. Calculations using the Block Localized Wavefunction decomposition method are used to understand the physical origins of this change. While the magnitudes of both the electric field and the electric field gradient at the Kr nucleus decrease upon addition of the CO to Kr-SO_3, the changes arise from different and rather complex combinations of geometrical distortion, electrostatic, polarization, and electron transfer effects. For the electric field gradient, polarization and structural change in the Kr-SO_3 make the primary contributions while for the electric field itself, the change in the electrostatic contribution has the largest effect. The calculated binding energies are additive, with that of the trimer very nearly equal to the sum of the binding energies of Kr-SO_3 and SO_3-CO.