CONCENTRATION DEPENDENCE OF THE PHOTOCHEMISTRY OF MATRIX-ISOLATED NITROMETHANE

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The concentration dependence of the photochemistry of matrix-isolated nitromethane and nitromethane-d_6 was studied. At higher concentrations, reactions involving fragments from adjacent parent molecules lead to photoproducts not observed in gas phase or dilute matrix studies. In particular, the isomeric forms of N_2O_4 lead to N_2O and a number of complexes, most notably $CO{\cdot}NO^+$ and $CO{\cdot}NO_3^-$. This effect is less pronounced when the deuterated compound is irradiated. Density functional theory calculations were used in the characterization of the observed photoproducts and the energetics of the pathways by which they were formed.