DEPENDENCE OF THE PHOTOFRAGMENTATION OF THE PERDEUTEROMETHOXY RADICAL ON THE C-O BOND EXTENSION

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Predissociation in the $\widetilde{A}^2A_1$ state of perdeuteromethoxy has been probed in a jet-cooled expansion by two techniques, fluorescence temporal decay and fluorescence depletion spectroscopy. The rate of photodissociation appears to not only be a function of total excitation energy but also of the vibrational mode excited. A threshold for the photodissociation is established at six quanta of the C-O stretch, ν_3. *Ab initio* calculations of the bond length extension as a function of each vibrational mode of this radical allows us to compare the absolute bond extension to the rate of photofragmentation. This comparison establishes a clear threshold for C-O bond extension to achieve bond fission. Similar results have been obtained for clearly related radicals CH_3O and CF_3S, where the C-X (X=O, S) bond breaking is again highly correlated with the extension of the C-X bond.