

The Photodissociation of Nitrosobenzene

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The absorption spectrum of the $S_0 \rightarrow S_2$ transition of ultracold nitrosobenzene in a supersonic jet was measured indirectly by monitoring the product yield of the NO fragment. The vibrational structure and relative line intensities are in very good agreement with the corresponding spectrum in an argon matrix. It is concluded that the yield of photofragmentation is constant for all vibronic S_2 -states up to an excess energy of 3500 cm^{-1} . The electronic origin line has Lorentzian lineshape with a homogeneous width of $(90 \pm 5) \text{ cm}^{-1}$. This corresponds to a lifetime of $\tau_2 = 60 \pm 3 \text{ fs}$.

Monomeric nitrosobenzene was cooled in a supersonic jet and photolyzed with a tunable laser by excitation into the first and second UV absorption bands corresponding to the second and higher excited singlet states (S_n , $n \geq 2$). The populations of the rotational and vibrational states of the NO fragment were probed by fluorescence excitation spectroscopy with a second laser. No alignment of the photofragment could be observed, and the Doppler profiles indicate an isotropic velocity distribution. It is concluded that the dissociation occurs after fast internal conversion to the potential energy surfaces of the electronic states S_0 or S_1 which correlate both with the electronic ground states of the products. A strong preference for the A'' component of the Λ -doublets is observed. If orbital symmetry is conserved, the plane of rotation of the NO fragment is perpendicular to the plane of the phenyl radical, i.e. dissociation occurs from a highly excited torsional state in a propeller-like motion.