MAGNETIC FIELD TUNING OF THE NO_2 PHOTODISSOCIATION THRESHOLD

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The lowest photodissociation threshold of NO_2, located at 25128.57±0.05 cm^{-1}, is now well characterized: below the threshold, the highly excited vibronic levels of NO_2, observed by LIF in a jet, have a lifetime of a few μsec; above the threshold, the resonant levels have a lifetime shorter than 10^2 psec and no fluorescence can be observed, because the molecule dissociates. The products, NO and O, are formed in their ground states: $NO_2(X^2A_1) + h\nu \rightarrow NO(^2\Pi_{1/2}) + O(^3P_2)$. We have studied by LIF the effect of a magnetic field on the dissociation threshold. The energy of the ground state of NO_2 (N=0, K=0, J=1/2) is lowered by $-\mu_B B$ for the M_S=1/2 component. The energy of the NO is unaffected (g≈0 for the $^2\Pi_{1/2}$ state), while the energy of the oxygen atom is splitted into 5 components (J=2). The lowest component, M_J=−2, which correspond to the energetic threshold, is lowered by $-3\mu_B B$, because the $^3P_2$ state has a Landé factor of 3/2. Consequently, we predict that the energy of the photodissociation threshold is lowered by $-2\mu_B B$. We have experimentally and quantitatively observed this effect: the photodissociation threshold observed by LIF is lowered by 13.2 cm^{-1} in a magnetic field of 14 Tesla! The fact that we have to consider only the energy of the upper levels (and not their quantum numbers) is a consequence of the strong mixing (chaos) within the rovibronic levels of NO_2 near the dissociation energy[a].

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[a]R.Georges, A.Delon and R.Jost, *J.Chem.Phys.* **103**, 1732 (1995). A.Delon, R.Georges and R.Jost, *J.Chem.Phys.* **103**, 7740 (1995).