

DISSOCIATION ENERGIES OF SIX NO_2 ISOTOPES

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We have measured the dissociation threshold energy, D_0 , ($NO_2 + h\nu \rightarrow NO(^2\Pi_{1/2}) + O(^3P_2)$) of the six NO_2 isotopologues made with ^{14}N or ^{15}N and ^{16}O or ^{18}O isotopes. These NO_2 isotopologues are cooled in a Helium supersonic jet at $T_{rot} \approx 2K$. For each isotopologue, the very dense set of bound $N = 1 K = 0$ rovibronic eigenstates is readily observed by LIF up to D_0 . Above D_0 , the LIF signal disappear abruptly, within $\pm 0.03cm^{-1}$ which is the average spacing between observed R_0 lines just below D_0 . Note that resonances (lifetime $\approx 10^{-10}$ sec.) located above D_0 can be observed in absorption (by CRDS) but no fluorescence can be detected from these. The six measured D_0 range from $25128.56cm^{-1}$ for $^{16}O^{14}N^{16}O$, noted (646), to $25171.80cm^{-1}$ for (858). At the B.O. approximation, these six D_0 should have a common D_e . The shifts between these six D_0 are due to the ZPE shifts of NO_2 and NO . We have used and check the following relation:

$$D_0(^xO^yN^zO) = D_e(NO_2) + \text{ZPE}(^yN^zO) - \text{ZPE}(^xO^yN^zO)$$

The ZPEs of the various NO and NO_2 isotopologues have been determined from Dunham parameters and, for NO_2 , also by Canonical Perturbation Theory (CPT) using two PESs of NO_2 . The NO_2 ZPE isotopologue shifts are estimated to be within $0.5cm^{-1}$. The uncertainties on ZPE of NO are significantly smaller. The six values of D_e are located within $0.5cm^{-1}$ around $26051.17cm^{-1}$, in agreement with the ZPE uncertainties.