



## Non-mass dependent photodissociation rates of ozone isotopologues from ab-initio absorption cross sections and experimental actinic flux

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The absorption cross sections (XSs) of eighteen isotopologues of the ozone molecule have been calculated in the range of the Chappuis-Huggins-Hartley bands:  $15000\text{--}55000\text{ cm}^{-1}$  with special emphasis to those of atmospheric interest: symmetric  $^{16}\text{O}_3$ ,  $^{16}\text{O}^{17}\text{O}^{16}\text{O}$ , and  $^{16}\text{O}^{18}\text{O}^{16}\text{O}$  and asymmetric  $^{17}\text{O}^{16}\text{O}_2$  and  $^{18}\text{O}^{16}\text{O}_2$ . We have used the MCTDH code which is based on the time propagation of the  $X(0,0,0)$  ground state initial wavepacket on the excited state PESs. The XSs have been obtained as the Fourier transform of the autocorrelation function of this wavepacket. The calculations have been performed only for zero total angular momentum and the rotational structure has been modeled numerically. The isotopologue dependence of the overall XSs has been characterized differently in each of the three bands: in the Chappuis band ( $15000\text{--}27000\text{ cm}^{-1}$ ) and in the Hartley band ( $33000\text{--}55000\text{ cm}^{-1}$ ), the XSs are weakly structured and the isotopologue dependence is globally weak. In contrast, in the Huggins band ( $27000\text{ to }33000\text{ cm}^{-1}$ ) the different XSs are highly structured and their peaks are significantly shifted from those of the  $^{16}\text{O}_3$  absolute XS which has been chosen as reference. The Hartley band of each isotopologue can be approximated by a bell shape envelop modeled by a modified Gaussian depending on only four parameters: amplitude, centre, width and asymmetry. The isotopologue dependence of the Hartley band resumes only into tiny differences between these parameters. The dependence of the Chappuis band is also weak. The isotopologue shifts of peaks in the Huggins bands induce a significant dependence of the photodissociation rates because these rates are the integral of the product of the XS by the actinic flux. Below 30 km, the actinic flux displays a tremendous attenuation in the range of the Hartley band because the solar flux is strongly absorbed by the stratospheric ozone, almost exclusively by the  $^{16}\text{O}_3$  isotopologue. This implies two consequences: a) the actinic flux reproduces (negatively and using a log scale because of the Beer-Lambert law) the XS of the  $^{16}\text{O}_3$  isotopologue, including its well pronounced vibronic structures in the range of the Huggins band; b) below typically 30 km, all the ozone isotopologues absorb (and are photodissociated) mostly in the range of their Huggins and the Chappuis bands. The  $J$  photodissociation rates of various ozone isotopologues may differ significantly because the dips in the actinic flux (these dips correspond to the vibronic structures of the  $^{16}\text{O}_3$  absolute XS) may not coincide with the maxima of the absolute XS of the various minor isotopologues. Quantitatively, the asymmetric isotopologues,  $^{17}\text{O}^{16}\text{O}_2$  and  $^{18}\text{O}^{16}\text{O}_2$ , are more efficiently photodissociated than their symmetric partners  $^{16}\text{O}^{17}\text{O}^{16}\text{O}$ , and  $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ . These differences between photodissociation rates reflect on the photodissociation oxygen isotope budget because the symmetric isotopologue  $^{16}\text{O}^{17}\text{O}^{16}\text{O}$ , (resp.  $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ ) leads only to one dissociation channel,  $^{16}\text{O}^{17}\text{O} + ^{16}\text{O}$  (resp.  $^{16}\text{O}^{18}\text{O} + ^{16}\text{O}$ ) and then only to  $^{16}\text{O}$  oxygen while the asymmetric isotopologue  $^{17}\text{O}^{16}\text{O}_2$  (resp.  $^{18}\text{O}^{16}\text{O}_2$ ) leads to two (almost equivalent) channels: either  $^{16}\text{O}^{17}\text{O} + ^{16}\text{O}$  or  $^{16}\text{O}^{16}\text{O} + ^{17}\text{O}$  (resp.  $^{16}\text{O}^{18}\text{O} + ^{16}\text{O}$  or  $^{16}\text{O}^{16}\text{O} + ^{18}\text{O}$ ) and then to about the same amount of  $^{16}\text{O}$  and  $^{17}\text{O}$  oxygen (resp. of  $^{16}\text{O}$  and  $^{18}\text{O}$ ). The  $J$  rates of various isotopologues, function of the altitude but averaged over other variables, will be presented.