

## Analysis of the Ultraviolet Absorption Cross Sections of Six Nitrous Oxide Isotopomers using 3D Wavepacket Propagation

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The loss of nitrous oxide from the atmosphere is very simple, involving photolysis in the stratospheric UV windows (90%);  $\text{N}_2\text{O} + h\nu \rightarrow \text{N}_2 + \text{O}(^1\text{D})$ .

In 1997 Yung and Miller presented the 'zero point energy' model [Yung and Miller, *Science* 1997, 278, 1778.], which revised our understanding of the role of photolysis in fractionating isotopomers. In this model the position of the absorption band of an isotopically substituted species is taken to be that of the main species shifted by the change in vibrational zero point energy. The ZPE model incorporates the invariance of the potential energy surfaces to isotopic substitution (Born-Oppenheimer approximation), and concludes that since the excited state is repulsive, increasing the vertical excitation energy by the ZPE change can approximate the isotope effect. Such a small shift of the band position would result in a significantly slower photolysis rate for heavy isotopomers, removing the imbalance in the isotopic budget and the need for exotic in situ sources. On the other hand, subsequent experiments showed isotopic enrichments about twice those predicted by the ZPE model [von Hessberg et al., *Atmos. Chem. Phys. Discuss.* 2004, 4, 2333], although qualitative agreement was observed.

In the present work, the ultraviolet absorption cross sections of six nitrous oxide isotopomers ( $^{14}\text{N}^{14}\text{N}^{16}\text{O}$ ,  $^{14}\text{N}^{14}\text{N}^{17}\text{O}$ ,  $^{14}\text{N}^{14}\text{N}^{18}\text{O}$ ,  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ ,  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ , and  $^{15}\text{N}^{15}\text{N}^{16}\text{O}$ ) were computed using the wave packet propagation technique to explore the influence of excited state dynamics, transition dipole surface and initial vibrational state. The wave packet propagation technique used here was the 'real wave packet' method [Gray and Balint-Kurti, *J Chem. Phys.* 1998, 108, 950]. The wave packet is represented using evenly spaced Fourier grids for R and r coordinates, and a associated Legendre polynomials based discrete variable representation (DVR) for the theta angle in Jacobi coordinates. The absorption potential used in the real wave packet propagation is taken as

[see my session. I can not write the equation here, sorry.], (1)

where  $x=R$ ,  $x_{\text{abs}}=7.0 \text{ a}_0$ , and  $C_{\text{abs}}=0.25$ , and where  $x=r$ ,  $x_{\text{abs}}=6.0 \text{ a}_0$ , and  $C_{\text{abs}}=0.25$ . To simulate the dissociation process induced by the photo-excitation, one must determine the initial wave packet correctly. In the time-dependent formulation, the product of the transition dipole moment function with the initial vibrational function of the electronic ground state gives the initial wave function.

[see my session. I can not write the equation here, sorry.], (2)

where  $\mu$  is the transition dipole moment function for the corresponding electronic transition, and  $\phi$  is the initial vibrational wave function of the electronic ground state. The resulting wave function is propagated on the potential energy surface (PES) of the electronically excited state. Finally the autocorrelation function was computed by numerically integrating the product of the initial wave packet and the evolving wave packet at each time step. Total photo-dissociation cross section as a function of the excitation energy was computed as the Fourier transform of the autocorrelation function as a function of time.

[see my session. I can not write the equation here, sorry.], (3)

where  $C_k$  is the order-dependent autocorrelation function in the Chebyshev order domain. In the present work, photo-dissociation cross sections were computed assuming the total angular momentum  $J=0$  and 1.

Numerous wave packet simulations were carried to calculate the photo-dissociation cross sections of the six isotopomers. The photolytic isotopic fractionation constants determined using the calculated cross sections are in good agreement with recent experiments (see my session, sorry.). If we have a time, we will talk about the comparison with the isovalent OCS.

