

# Photodissociation of N<sub>2</sub>O

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## Abstract

Adiabatic potential energy surfaces for the six lowest singlet electronic states of N<sub>2</sub>O ( $X^1A'$ ,  $2^1A'$ ,  $3^1A'$ ,  $1^1A''$ ,  $2^1A''$  and  $3^1A''$ ) have been computed using an *ab initio* multi-reference configuration interaction (MRCI) method and a large orbital basis set (aug-cc-pVQZ). The potential energy surfaces display several symmetry related and some non-symmetry related conical intersections. Total photodissociation cross sections and product rotational state distributions have been calculated for the first ultraviolet absorption band of the system using the adiabatic *ab initio* potential energy and transition dipole moment surfaces corresponding to the lowest three excited electronic states. In the Franck-Condon region the potential energy curves corresponding to these three states lie very close in energy and they all contribute to the absorption cross section in the first ultraviolet band. The total angular momentum is treated correctly in both the initial and final states. The total photodissociation spectra and product rotational distributions are determined for N<sub>2</sub>O initially in its ground vibrational state (0,0,0) and in the vibrationally excited (0,1,0) (bending) state. The resulting total absorption spectra are in good quantitative agreement with the experimental results over the region of the first ultraviolet absorption band, 160 nm to 220 nm. All of the lowest three electronically excited states [ $^1\Sigma^-(1^1A'')$ ,  $^1\Delta(2^1A')$  and  $^1\Delta(2^1A'')$ ] have zero transition dipole moments from the ground state [ $^1\Sigma^+(1^1A')$ ] in its equilibrium linear configuration. The absorption becomes allowed only through the bending motion of the molecule. The  $^1\Delta(2^1A') \leftarrow X^1\Sigma^+(1^1A')$  absorption dominates the absorption cross section with absorption to the other two electronic states contributing to the shape and diffuse structure of the band. It is suggested that absorption to the bound  $^1\Delta(2^1A'')$  state makes an important contribution to the experimentally observed diffuse structure in the first ultraviolet absorption band. The predicted product rotational quantum state distribution at 203 nm agrees well with experimental observations.