Near-Threshold, Vibrationally-Resolved Photoionization of Molecular Nitrogen

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Photoionization of molecular nitrogen (N$_2$) is investigated near the first ionization threshold using an R-matrix, multi-channel quantum defect theory (MQDT) approach. Building on an existing fixed-nuclei R-matrix photoionization model [M. Tashiro, J. Chem. Phys. 132, 134306, (2010)], which, in turn, is built on the UKRmol suite of codes, photoionization cross sections, as well as scattering and dipole matrices, are computed in the Born-Oppenheimer approximation. By varying the internuclear separation, potential energy curves have been constructed for the N$_2$ and N$_2^+$ states and compared to quantum chemistry calculations. Using these fixed-nuclei potential energy curves, and corresponding vibronic eigenenergies and eigenfunctions, a frame transformation is enacted on the fixed-nuclei scattering and dipole matrices, allowing for the calculation of vibrationally-resolved photoionization cross sections. The resultant photoionization cross sections are compared to high-resolution experimental data [P. O’Keeffe et al. J. Chem. Phys 136, 104307, (2012)] near threshold, a region complicated by multiple vibrationally-resolved, interacting Rydberg series.