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Interactive comment on "Isotope effects in N_2O photolysis from first principles" *by* J. A. Schmidt et al.

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The paper of Schmidt *et al.* is interesting and merits publication. It is, we believe, an excellent example of a benchmark calculation, serving both in its own right and in testing a common approximation used for treating electronic spectra, in the present case the Franck-Condon principle used by Chen *et al*., (2010) to treat isotopic fractionation. We will submit a detailed discussion of the comparison elsewhere, but as the authors point out, the agreement is good. We are not aware of any previous benchmark computational test of the Franck-Condon principle for isotopic fractionationof a triatomic molecule. We note that there are at least threeversions of this principle (Heller, 1978 and Schinke 1993; Lee *et al*. 1983; Chen *et al*. 2008), differing somewhat in their treatment of the potential energy and zero-point energy of the ground state. We used the

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actual potential energy difference of the ground and excited states (Chen *et al*. 2008, 2010). This method (Chen *et al*. 2008, 2010) conservespositions of atoms and momenta during a transition, as in the original Condon approach (Condon, 1928; Berry *et al*., 2000), andweights each value of the coordinates in accordance with the square of the amplitude of the molecular wavefunction in each initial quantum state.This form of the Franck-Condon principle is also the starting point of a systematic quantum mechanical spectral moment perturbation treatment of the Franck-Condon principle (Sovkov and Ivanov, 1998).

The question of adjustable parameter enters. In neither case were any adjustable parameters derived from isotopic fractionation data employed. In Schmidt *et al*. (2011), there was an adjustment (a shift of 300 cm^{-1}) to match oscillations in the spectrum and an adjustment of the peak intensityby a factor of 1.4to match the absolute absorption intensity, and in our case, with a less refined pair of potential energy surfaces, there was an adjustment of peak height (a factor of 1.6) and a shift of the absorptionspectral peak (a shift of 800 cm^{-1}) to match the experimental absorption spectrum. For neither paper, in our view,does the term "semi-empirical" appropriately characterize both papers on that account, although that terminology isappropriatefora situation whereisotopic fractionation data are used tofit other isotopic fractionation data. There is some parallel in numerous other topics, for example in the calculation of electron transfer rates or rates of unimolecular reactions, where existing thermodynamic data are used, in conjunction with computations or approximate analytic theory to compute reaction rates, rather than calculate everything *ab initio*.

Both the present paper (Schmidt *et al*, 2011) and previous work (Chen *et al*. 2010) do not treat specifically the rotations of the molecule. In some systems, such as NO_2, Coriolis and other rotational effects can play a role (Bezel *et al*., 1999) and, for a benchmark calculation, an extension that includes rotational coordinates would be needed. In the meanwhile, however, the present article serves as a double accomplishment, the treatment of isotopic fractionation itself and a test of the Franck-Condon principle

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for N_{2O} for that purpose, and merits publication.

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