The photoelectron spectrum of the C2H anion was simulated using a quasidiabatic Hamiltonian of the type advocated by Koeppel, Domcke and Cederbaum (KDC, reference here). In this approach, the Hamiltonian is represented in a basis of quasidiabatic (slowly varying) electronic states for which the kinetic energy operator can be assumed diagonal. For C2H, the KDC Hamiltonian comprises three states – the two components of the 2PI state and the ground 2SIGMA state -- and is then projected onto a vibrational basis, usually chosen as a direct product of harmonic oscillators. Diagonalization of the corresponding matrix yields the molecular states (which are given in terms of a Born-Huang expansion), and the squared projections of the corresponding eigenvectors onto the ground state of the anion yield the relative intensities. The latter is automatically true if the photodetachment cross sections for the 2SIGMA and 2PI states are assumed equal, but different cross sections of the two states can be incorporated by scaling the intensities of states according to their (vibronic) symmetry.

Details of the construction and parametrization of KDC Hamiltonians can be found elsewhere in the literature (references), and the procedure followed will be discussed here only briefly. The present calculations use the so-called quadratic vibronic coupling (QVC) model. For the system at hand, the QVC model Hamiltonian assumes the following form

(handwritten equation #1)

where the summations run over the dimensionless normal modes (qi) that serve as the coordinate system for the problem. For convenience, the latter are chosen to be those of the anion, which considerably facilitates calculation of the spectral intensities. In Eq. 1, the diagonal terms of V (excluding those that carry the Renner-Teller coupling constant h) represent the quasidiabatic potential energy surfaces of the SIGMA, and the two components of the PI state, chosen here as those in which the unpaired electron lies within or is perpendicular to an arbitrarily chosen plane, designated as A(a’) and A(a’’), respectively. DELTA\_0^X is the separation of the anion and SIGMA states at the origin of the coordinate system (the vertical electron detachment energy), and DELTA\_0^PI is the gap between anion and PI states at the same geometry.

For the modes of sigma symmetry (q1 and q3), the diabatic forces (F\_i) and force constants (F\_ij) coincide with those of the adiabatic potential energy surfaces. However, for the bending mode, the diabatic (F22) and adiabatic (f22) force constants differ, and the parametrization is somewhat more involved. For each component of the PI state, either the 2a or 2b component of the bending vibration will maintain the A’ electronic symmetry that is needed to couple with the X state. Designating these as 2a for the A(a’) state and 2b for the A(a’’) state (as is implicit in Eq. 1), the diabatic force constants for the bending mode in the X and A states can be written as

(handwritten equation #2)

where the Renner-Teller interaction strength (h) is determined from

(handwritten Eq. 3)

once the interstate coupling (l, which is calculated analytically in this work, see below) is known.

When the potential in Eq. 1 is diagonalized, the adiabatic states that are used for its parametrization are precisely recovered through second order in displacement.

To parametrize this Hamiltonian, the equation-of-motion coupled-cluster method known as EOMIP-CCSDT has been used … (Zach goes from here)…