Vibrational Transition Moments and Dipole Derivatives

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November 9, 2006

Oscillator strengths and integrated absorption intensities of simple vibrational absorption (infrared) spectra are related to the squares of electric-dipole transition moments, \(^1\)

\[
D_{nv}^n = \langle \Psi_{nv} | \hat{\mu} | \Psi_{nv'} \rangle \cdot \langle \Psi_{nv'} | \hat{\mu} | \Psi_{nv} \rangle,
\]

where \(n\) denotes the electronic state, \(v\) and \(v'\) denote vibrational states, and \(|\Psi_{nv}\rangle\) and \(|\Psi_{nv'}\rangle\) denote initial and final vibronic states, respectively.

We may compute the electric-dipole vibrational transition moment beginning from the Born-Oppenheimer approximation, in which we assume that the total vibronic wave function, \(\Psi_{nv}(r, R)\), may be written as a product of an electronic wave function, \(\psi_n(r; R)\) and a vibrational wave function, \(\chi_{nv}(R)\), where \(r\) and \(R\) denote the collective electronic and nuclear coordinates, respectively. Then the electric-dipole transition matrix element may be written as

\[
\langle \Psi_{nv}(r, R) | \hat{\mu} | \Psi_{nv'}(r, R) \rangle = \langle \chi_{nv}(R) | \langle \psi_n(r; R) | \hat{\mu} | \psi_n(r; R) \rangle | \chi_{nv'}(R) \rangle = \langle \chi_{nv} | \langle \hat{\mu} \rangle_n | \chi_{nv'} \rangle
\]

where \(\langle \hat{\mu} \rangle_n\) denotes the expectation value of the electric-dipole operator in the \(n\)-th Born-Oppenheimer electronic state. The dependence of the \(\langle \hat{\mu} \rangle_n\) on the nuclear coordinates is usually approximated by the first term of its Taylor expansion about a reference geometry \(R^0\) (i.e., the electrical harmonic approximation):

\[
\langle \hat{\mu} \rangle_n \approx \langle \hat{\mu} \rangle_0 + \sum_{\alpha} \left( \frac{\partial \langle \hat{\mu} \rangle_n}{\partial R_\alpha} \right)_0 (R_\alpha - R^0_\alpha),
\]

where the subscript \(0\) indicates that the given quantity is evaluated at the reference geometry. The dipole-moment derivatives may be easily computed using analytic gradient techniques, and the final expressions vary depending on the level of theory employed.\(^2\) The total electric-dipole transition matrix element then becomes

\[
\langle \Psi_{nv} | \hat{\mu} | \Psi_{nv'} \rangle = \sum_{\alpha} \left( \frac{\partial \langle \hat{\mu} \rangle_n}{\partial R_\alpha} \right)_0 \langle \chi_{nv} | (R_\alpha - R^0_\alpha) | \chi_{nv'} \rangle.
\]

The vibrational wave functions, \(\chi_{nv}\), are usually taken to be harmonic oscillator functions (i.e., the mechanical harmonic approximation), which subsequently leads to relatively simple programmable equations in terms of the normal vibrational modes.\(^3\)

References

