Vibrational Transition Moments and Dipole Derivatives

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

$$D_{vv'}^n = \langle \Psi_{nv}|\hat{\mu}|\Psi_{nv'}\rangle \cdot \langle \Psi_{nv'}|\hat{\mu}|\Psi_{nv}\rangle, \tag{1}$$

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, $\Psi_{nv}(\mathbf{r}, \mathbf{R})$, may be written as a product of an electronic wave function, $\psi_n(\mathbf{r}; \mathbf{R})$ and a vibrational wave function, $\chi_{nv}(\mathbf{R})$, where $\mathbf{r}$ and $\mathbf{R}$ denote the collective electronic and nuclear coordinates, respectively. Then the electric-dipole transition matrix element may be written as

$$\langle \Psi_{nv}(\mathbf{r}, \mathbf{R})|\hat{\mu}|\Psi_{nv'}(\mathbf{r}, \mathbf{R})\rangle = \langle \chi_{nv}(\mathbf{R})|\langle \psi_n(\mathbf{r}; \mathbf{R})|\hat{\mu}|\psi_n(\mathbf{r}; \mathbf{R})\rangle|\chi_{nv'}(\mathbf{R})\rangle = \langle \chi_{nv}|\langle \hat{\mu}\rangle_n|\chi_{nv'}\rangle \tag{2}$$

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 $\mathbf{R}^0$ (*i.e., the electrical harmonic approximation*):

$$\langle \hat{\mu}\rangle_n \approx \langle \hat{\mu}\rangle_0 + \sum_\alpha \left(\frac{\partial \langle \hat{\mu}\rangle_n}{\partial R_\alpha}\right)_0 (R_\alpha - R_\alpha^0), \tag{3}$$

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

$$\langle \Psi_{nv}|\hat{\mu}|\Psi_{nv'}\rangle = \sum_\alpha \left(\frac{\partial \langle \hat{\mu}\rangle_n}{\partial R_\alpha}\right)_0 \langle \chi_{nv}|(R_\alpha - R_\alpha^0)|\chi_{nv'}\rangle. \tag{4}$$

The vibrational wave functions, χ_{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

[1] L. D. Barron, *Molecular Light Scattering and Optical Activity*, 2nd edition ed. (Cambridge University Press, Camridge, U.K., 2004).

[2] Y. Yamaguchi, Y. Osamura, J. D. Goddard, and H. F. Schaefer, *A New Dimension to Quantum Chemistry: Analytic Derivative Methods in* Ab Initio *Molecular Electronic Structure Theory*, No. 29 in *International Series of Monographs on Chemistry* (Oxford Univ. Press, New York, 1994).

[3] E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra* (Dover, New York, 1980).