Chem 740/7400

"Methods of Theoretical Spectroscopy for Determination of Intermolecular Potentials"

Spring 2011 **Instructor: R.J. Le Roy** **READING COURSE**

The patterns of energy levels and transition intensities observed in molecular spectra have always been key tools for understanding molecular structure and properties, for fingerprinting and identifying unknown species, and for monitoring the concentrations of particular molecular states during chemical reactions. These patterns are determined mainly by the nature of the potential energy curves or surfaces characterizing the forces between the component atoms. This course will discuss the origin and nature of such potentials, the way in which they determine the spectroscopic properties of a molecule, methods for calculating such properties, and the inversion problem of determining potentials (and transition moment functions) from experimental data. While the specific content deals only with diatomic molecules, the essential principles also apply to polyatomic systems. The course will also introduce some widely used practical computational tools for performing such calculations, and will provide opportunities to work with standard programs for calculating discrete and continuum spectra and determining potentials from experimental data. Topics to be addressed include:

1. Origin of and Models for Interaction Potentials
   - The Born-Oppenheimer Separation: A summary of the theory and exact treatment of simple diatomic molecules
   - Perturbation Theory Description of Long-Range Forces
   - Potential Models
     - analytic one-dimensional model potentials (and their deficiencies)
     - "HFD"-type models
     - "MLR" models
2. Quantum Mechanical Treatment of Discrete Level Properties and Spectra
   - the nature of vibration-rotation energy levels
   - exact quantal calculations for an arbitrary potential
   - centrifugal distortion constants and other properties, their nature and calculation
   - intensities and Franck-Condon factors for discrete transitions
3. Semiclassical Treatment of Discrete Level Properties and Spectra
   - the semiclassical or WKB approximation in first- and higher-order
   - the Dunham series and related theory
   - centrifugal distortion constants, their nature and calculation
   - "near-dissociation theory" and its implications
4. Bound State Inversion Procedures
   - the semiclassical "RKR" inversion procedures
   - quantum mechanical "direct potential fit" (DPF) inversion procedures
5. Continuum Levels and Spectra: Photodissociation, Predissociation & Bound→Continuum Emission
   - the nature and normalization of continuum wave functions
   - bound → continuum transition intensities, and their exact and approximate calculation
   - photodissociation cross sections (continuum absorption coefficients), emission and predissociation
   - general direct-fit inversion procedures

- semiclassical inversion of oscillatory bound → continuum intensities
- continuum-continuum (or collision-induced) spectra

6. Non-Mechanical Behaviour
   - Born-Oppenheimer breakdown
   - curve crossings and diabatic *vs.* adiabatic behaviour
   - perturbations and predissociation

Requirements

The course grade will be based on problem assignments and a final written exam. Some of the assignments will involve the use of computer programs for simulating or inverting spectral data. However, extensive computer experience *is NOT* assumed, and tutorial assistance will be provided as required. (In particular, all a student is required to do is to use some editor (such as *vi* or *pico* or *WORD* or *EMACS*) to prepare an input data file, and then type the requisite "run" command.) Accounts will be provided on an appropriate computer (*scienide*), although the programs in question may also be downloaded and run on PC's with good Fortran compilers.

The background assumed is a year of calculus, some familiarity with what differential equations are, and a basic one-semester course in quantum mechanics. While additional background in spectroscopy would be useful, it is not essential.

Reference Materials

There is no single reference adequate or appropriate to act as a required text for this course. However, illustrative figures and printed notes for some segments of the course and will be distributed. Relevant reference materials are listed below.[1–10]

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[1] J. O. Hirschfelder and W. J. Meath, in *Intermolecular Forces*, Vol. 12 of *Adv. Chem. Phys.*, edited by J. O. Hirschfelder (Interscience, New York, 1967), Chap. 1, pp. 3–106.

[2] E. A. Mason and L. Monchick, in *Intermolecular Forces*, Vol. 12 of *Adv. Chem. Phys.*, edited by J. O. Hirschfelder (Interscience, New York, 1967), Chap. 7, pp. 329–387.

[3] R. J. Le Roy, in *Molecular Spectroscopy*, edited by R. Barrow, D. A. Long, and D. J. Millen (Chemical Society of London, London, 1973), Vol. 1, Specialist Periodical Report 3, pp. 113–176.

[4] R. J. Le Roy, in *Semiclassical Methods in Molecular Scattering and Spectroscopy*, Vol. 53 of *Series C - Mathematical and Physical Sciences*, edited by M. Child (D. Reidel, Dordrecht, 1980), pp. 109–126.

[5] G. C. Maitland, M. Rigby, E. B. Smith, and W. A. Wakeham, *Intermolecular Forces - Their Origin and Determination* (Oxford University Press, Oxford, UK, 1981).

[6] J. N. Murrell *et al.*, *Molecular Potential Energy Functions* (Wiley, New York, 1984), .

[7] J. Tellinghuisen, in *Photodissociation and Photoionization*, Vol. 60 of *Adv. Chem. Phys.*, edited by K. P. Lawley (John Wiley & Sons Ltd., New York, 1985), pp. 299–369.

[8] D. M. Hirst, *Potential Energy Surfaces* (Taylor and Francis, 1985), .

[9] M. Rigby, E. B. Smith, W. A. Wakeham, and G. C. Maitland, *The Forces Between Molecules* (Oxford University Press, Oxford, U.K., 1986).

[10] H. Lefebvre-Brion and R. W. Field, *Perturbations in the Spectra of Diatomic Molecules* (Academic Press, New York, 1986).