5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

Lecture # 23 Supplement

See Microwave Spectroscopy by C. H. Townes and A. L. Schawlow, Dover Publications, New York (1975) for complete text of these Appendices.

Contents

A. Appendix III: Coefficients for Energy Levels of a Slightly Asymmetric Top, pp. 522-526

SUMMARY

Rotational energy is given by

$$w = K^2 + C_1 b + C_2 b^2 + C_3 b^3 + C_4 b^4 + C_5 b^5 + \ldots$$

$$\text{For a prolate top, energy } = W = \frac{B+C}{2} J(J+1) + \left(A - \frac{B+C}{2}\right) w$$

$$b = b_p = \frac{C-B}{2A-B-C}$$

$$\text{For an oblate top, energy } = W = \frac{A+B}{2} J(J+1) + \left(C - \frac{A+B}{2}\right) w$$

$$b = b_o = \frac{A-B}{2C-B-A}$$

Where the first few constants K, C_1, $C_2 \ldots$ are identical for pairs of degenerate levels. They are usually listed for only the first of the two levels. (C_1, C_2, and C_3 were computed by J. F. Lotspeich; C_4 and C_5 by J. Kraitchman and N. Solimene.)

B. Appendix IV: Energy Levels of a Rigid Rotor, pp. 527-555

SUMMARY

Energy (in Hz) = $W/h = \frac{1}{2}(A+C)J(J+1) + \frac{1}{2}(A-C)E_\tau$. E_τ is tabulated as a function of the rotational level $J_{K_{-1}K_1}$ (or J_τ) and of the asymmetry parameter $\kappa = \frac{2B-A-C}{A-C}$.

Values for positive κ only are tabulated, since those for negative κ can be obtained from the relation $E_\tau(\kappa) = -E_{-\tau}(-\kappa)$. For further explanation see Chapter 4.

This table was reproduced with the permission of the Ballistics Research Laboratories, Aberdeen, MD, from *Ballistics Research Laboratories Report* No. 878 (September, 1953), by T. E. Turner, B. L. Hicks, and G. Reitwiesner. It was prepared for reproduction by S. Poley with the aid of an IBM card-controlled typewriter at the Watson Scientific Computing Laboratory.

Tables of E_τ for J up to 40 and values of $\kappa = 0, 0.1, 0.2, 0.3, \ldots 1.0$ are given by G. Erlandsson, *Arkiv för Fysik* **10**, 65-88 (1956).

C. Appendix V: Transition Strengths for Rotational Transitions, pp. 557-559

SUMMARY

Intensity of a transition between rotational levels J_{kl} and J'_{mn} is proportional to

$$(\mu_x)^2\ {}^xS_{J_{kl}J'_{mn}}(\kappa) = (2J+1)\left|(\mu_x)_{J_{kl}J'_{mn}}\right|^2$$

Here μ_x is the dipole moment along one of the principal axes of inertia ($x = a, b$ or c), and S is the quantity tabulated here as a function of initial and final state and of the asymmetry parameter κ. However, each value has been multiplied by 10^4 to eliminate decimal points. The upper sign for values of K applies to transition subbranches listed in the two left-hand columns, and the lower sign to those in the right-hand columns. The axis along which a dipole moment is required to produce a given transition is indicated by a superscript to the left of the subbranch designation. Thus ${}^cQ_{10}$ indicates a Q branch ($\Delta J = 0$) with a change in K_{-1} of 1, a change in K_1 of 0, and that a dipole moment μ_c along the c axis is required for the transition. For further discussion see Chapter 4. [Tables in this appendix are taken from P. C. Cross, R. M. Hainer, and G. W. King, *J. Chem. Phys.* **12**, 210 (1944).]