

NOTE

Where Is the Intensity Maximum in a Pure Rotational Spectrum?

I. INTRODUCTION

Most spectroscopy textbooks discuss rotational intensity distributions of molecular spectra in the context of pure rotational or microwave spectra, where explicit or implicit statements that “line intensities are directly proportional to the population (and) will be a maximum near the J value for the most populated level” (J), or “apart from depending on . . . which varies relatively little with J , intensities depend on the population of the lower state of a transition” (2), tend to appear. However, this ignores the transition–frequency factor which also contributes to absorption and emission intensities, and the fact that in absorption the intensity actually depends on the population difference between the lower and upper levels of the transition. The simple derivations presented below show that for a linear rigid rotor these factors give rise to very substantial shifts of the J value for the associated intensity maxima (relative to that for the most populated rotational level). Analogous shifts will clearly also occur for nonlinear molecules.

II. THE THERMAL POPULATION DISTRIBUTION

For a simple linear rigid rotor, the level energies are given by the expression

$$F_v(J) = B_v J(J + 1), \quad [1]$$

where B_v is the inertial rotational constant for vibrational level v , and J is the rotational quantum number. Taking account of the rotational degeneracy, the thermal equilibrium population distribution over the rotational sublevels at temperature T is then proportional to the factor

$$f_T(J) = (2J + 1)e^{-F_v(J)/k_B T}, \quad [2]$$

where k_B is Boltzmann’s constant. Substituting Eq. [1] into Eq. [2] and taking the derivative with respect to J and setting it equal to zero then gives the familiar expression for the J value associated with the maximum in the thermal population distribution (1–4),

$$J_{\max}^{\text{therm}}(T) = \sqrt{k_B T / 2B_v} - \frac{1}{2}. \quad [3]$$

III. ABSORPTION

In a pure rotational absorption spectrum where $\Delta J = +1$, the Hönl–London rotational linestrength factor for a linear molecule with no electronic angular momentum projection along the molecular axis is $(J + 1)$, where J is the lower or initial state rotational quantum number. The intensities in this spectrum then depend on a combination of this factor with the product of the transition frequency $\nu(J) = 2B_v(J + 1)$ and the population difference between the upper (J') and lower states of the transition, or more explicitly

$$I_{\text{abs}}(J) \propto \frac{J + 1}{2J + 1} \nu(J) f_T(J) [1 - e^{-[F_v(J') - F_v(J)]/k_B T}] \\ \propto 2B_v(J + 1)^2 e^{-B_v J(J+1)/k_B T} [1 - e^{-2B_v(J+1)/k_B T}]. \quad [4]$$

Taking the derivative of this expression with respect to J and setting the result equal to zero yields

$$(2J + 1)^2 \frac{B_v}{k_B T} = 4 - \frac{2}{J + 1} + \frac{(4J + 2)B_v/k_B T}{e^{2(J+1)B_v/k_B T} - 1}. \quad [5]$$

If the rotational spacing $2(J + 1)B_v \gg k_B T$, the last term in Eq. [5] becomes negligible and this expression yields the familiar result of Eq. [3]. However, in the more usual case where the rotational level spacing $2(J + 1)B_v < k_B T$, the exponential on the right-hand side of Eq. [5] may be expanded in a Taylor series, yielding

$$(2J + 1)^2 B_v/k_B T = 6 - 3/(J + 1) - (2J + 1)B_v/k_B T + \dots \quad [6]$$

Thus, in the usual case of $2(J + 1)B_v \ll k_B T$, we obtain the result that the J value associated with the maximum in the pure rotational absorption spectrum is approximately

$$J_{\max}^{\text{abs}}(T) = \left(\frac{3k_B T}{2B_v} \right)^{1/2} \left[1 - \frac{1}{2(J + 1)} - \frac{(J + 1/2)B_v}{3k_B T} + \dots \right]^{1/2} - \frac{1}{2} \\ \approx \sqrt{3} J_{\max}^{\text{therm}}(T). \quad [7]$$

IV. EMISSION

In a pure rotational emission spectrum where $\Delta J = -1$ and there is (again) no electronic angular momentum along the molecular axis, the rotational linestrength factor written in terms of the initial or upper state rotational quantum number (J') is simply a factor of J' . The emission intensity (in units, energy per unit time) then depends on a combination of this factor with a product of the initial state population times the fourth power of the emission frequency $\nu(J') = 2J'B_v$ as follows:

$$I_{\text{em}}(J') \propto \frac{J'}{2J' + 1} \nu(J')^4 f_T(J') = 8(B_v)^4 (J')^5 e^{-B_v J'(J'+1)/k_B T}. \quad [8]$$

Taking the derivative of this expression with respect to J' and setting the result equal to zero yields

$$(2J' + 1)^2 B_v/k_B T = 10 + 5/J', \quad [9]$$

which in turn yields an expression for the J' value associated with the intensity maximum in the pure rotational emission spectrum of a linear rigid rotor. Since all transitions in pure rotational spectra are $R(J)$ lines labeled by the lower state quantum number $J = J' - 1$, in terms of the latter this yields

$$J_{\max}^{\text{em,E}}(T) = \left(\frac{5k_B T}{2B_v} \right)^{1/2} \left[1 + \frac{1}{2(J + 1)} \right]^{1/2} - \frac{3}{2} \approx \sqrt{5} J_{\max}^{\text{therm}}(T). \quad [10]$$

Note, however, if the experiment uses a detector which counts the emitted

photons (as does a photoelectric detector) rather than measuring their energies, the factor $\nu(J')^4$ in Eq. [8] is replaced by $\nu(J')^3$ and Eq. [10] becomes

$$J_{\max}^{\text{em,N}}(T) = \left(\frac{2k_{\text{B}}T}{B_{\nu}} \right)^{1/2} \left[1 + \frac{1}{2(J+1)} \right]^{1/2} - \frac{3}{2} \approx 2J_{\max}^{\text{therm}}(T). \quad [11]$$

V. DISCUSSION

The numerical correction factors derived above can give rise to very substantial changes in the predicted J value associated with the intensity maximum. For example, for ground state CsI at room temperature, the thermal population maximum lies at $J = 65$, but the intensity maximum for absorption lies at $J_{\max}^{\text{abs}} = 113$ and that for emission at $J_{\max}^{\text{em,E}} = 146$ or $J_{\max}^{\text{em,N}} = 130$. For lighter molecules the absolute differences in the various J_{\max} values are of course smaller, but the relative differences are approximately the same.

These factors have an even more dramatic effect when one attempts to use the position of an observed intensity maximum to determine the experimental temperature. For example, Bernath's Fig. 6.14 (4) shows a high-temperature pure rotational HF emission spectrum with its intensity maximum at $J = 19$. Converting this result to an effective temperature using the thermal population expression of Eq. [3] would imply $T = 22,500$ K, while use of Eq. [11] yields a somewhat more plausible $T = 6,060$ K. In this particular case, the wavenumber dependence of the sensitivity of the spectrometer and detector were not calibrated and used to correct these results (5), so the latter value is still substantially higher than the actual experimental temperature of 1,600 K (6). However, this does not belie the factor of four difference between the temperature predictions yielded by Eqs. [3] and [11].

In spite of the simplicity of the above derivations, most standard sources overlook the very substantial deviation of the pure rotation intensity distribution from the thermal population distribution. Partial exceptions include Herzberg's diatomic book (3) and Hollas's "big" book (7). In particular, Herzberg notes that the factors of $\nu(J)$ for absorption and $\nu(J)^4$ for emission cause $J_{\max}^{\text{therm}}(T)$ to be multiplied by factors of $\sqrt{2}$ and $\sqrt{5}$, respectively (3). The latter corresponds to the current result of Eq. [10], but the former differs from Eq. [7] because of his neglect of the population difference factor in Eq. [4]. Hollas notes that the population difference factor of Eq. [4] produces "... a maximum in the absorption intensity at a higher J -value than $J_{\max}^{\text{therm}}(T)$," but he does not report the analytical result of Eq. [7] and does not discuss the peak shift in emission (7). In addition, Gordy and Cook (8) present a numerical factor which is approximately equivalent to Eq. [4], but do not give an explicit analytical expression.

The shifts of the pure rotation absorption and emission intensity distributions from the thermal population distribution will of course not occur in vibrational or electronic spectra, because the large vibrational and/or electronic contributions to the transition frequencies will mask the J dependence discussed herein. These displacements will also not occur in pure rotational Raman spectra, because the two-photon nature of that process decouples the simultaneous $\Delta J = \pm 2$ Stokes and anti-Stokes processes, while the fact that the Rayleigh frequency is very much larger than the rotational spacings makes the effect of the J dependence of the $\nu(J)^4$ scattering intensity factor negligible. On the other hand, while analogous closed form expressions are not so readily worked out, these considerations clearly also give rise to substantial shifts of intensity maxima from the thermal distributions in pure rotational spectra of nonlinear molecules.

REFERENCES

1. C. N. Banwell, "Fundamentals of Molecular Spectroscopy", 2nd ed., McGraw-Hill, Maidenhead, UK, 1972.
2. J. M. Hollas, "Modern Spectroscopy", 3rd ed., Wiley, Chichester, UK, 1996.
3. G. Herzberg, "Spectra of Diatomic Molecules", Van Nostrand, Toronto, 1950.
4. P. F. Bernath, "Spectra of Atoms and Molecules," Oxford Univ. Press, Oxford, UK, 1995.
5. P. F. Bernath, private communication, 1998.
6. H. G. Hedderich, K. Walker, and P. F. Bernath, *J. Mol. Spectrosc.* **149**, 314–316 (1991).
7. J. M. Hollas, "High Resolution Spectroscopy," Butterworth, London, UK, 1982.
8. W. Gordy and R. L. Cook, "Microwave Molecular Spectroscopy," Interscience, New York, 1970.

Robert J. Le Roy

*Guelph-Waterloo Centre for Graduate Work in Chemistry
University of Waterloo
Waterloo, Ontario N2L 3G1
Canada*

Received April 28, 1998; in revised form July 9, 1998