01 Jan 1985

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Recommended Citation

R. J. Bieniek, "Erratum: Normalized Line Shapes For Far-wing Continuum Spectra: The Rb-Xe Satellite Band (Physical Review A(1985) 32, 5 (3150-3152))," *Physical Review A*, vol. 32, no. 5, pp. 3150 - 3152, American Physical Society, Jan 1985.
The definitive version is available at https://doi.org/10.1103/PhysRevA.32.3150

RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 32, NUMBER 5 NOVEMBER 1985

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Normalized line shapes for far-wing continuum spectra: The Rb-Xe satellite band

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(Received 22 April 1985)

Recent advances in experimental spectroscopy offer the promise of yielding much detailed information about molecular potentials and collisional interactions from a study of the light emitted or absorbed in the far wings of atomic lines. However, readily manipulable, accurate theoretical expressions and methods are needed to extract such knowledge. Straightforward formulas, based on the distorted-wave approximation, for the normalized emission intensity in the far wing of a pumped atomic line are given here. By normalizing theoretical spectra with respect to the strength of the atomic line, one obtains a convenient form for the analysis of experimental differential spectra that are reported in nonarbitrary units. Theoretical and experimental spectra are numerically consistent in the test case of the blue-wing satellite (~ 7610 Å) of the Rb D_2 line (7800 Å) broadened by Xe perturbers.

Many advances have recently been made in experimental measurements of collisionally redistributed polarized light[1] and far-wing spectra, both at infrared[2,3] and synchrotron wavelengths,[4] and even in molecular reactions.[5] This includes the numerical determination of emission intensities and absorption coefficients of resolved interference structure associated with spectral satellites of atomic lines[4,6-8] and avoided crossings.[9] Analogous rainbow phenomenon has been observed in the energy spectrum of electrons ejected in Penning ionization.[10] In a previous paper, an analytic semiclassical method of computing far-wing spectra was presented, and shown to be in excellent agreement with quantal results.[11] However, it was not compared intimately with experiment. In particular, the intensity scale was given in infamous arbitrary units, which has been the prevalent manner when comparing theory with experiment. The transition dipole moment can always be adjusted in computations until acceptable intensity agreement is achieved, but this assumes the rest of the elements in theoretical formulas are given correctly or evaluated accurately. A more direct test is presented here. The overall accuracy of a theoretical expression needs to be verified in relatively simple cases if it is to be trusted in more complex situations. These are now arising as more energetic states are becoming experimentally accessible.

Hedges, Drummond, and Gallagher pioneered a simple method of reporting experimental far-wing spectral intensities that is amenable to theoretical analyses.[12] One defines a normalized differential emission intensity ($dI_N/d\omega$) as the ratio of the differential intensity per unit volume ($dI/d\omega$) per unit perturber density (n_p) and the total integrated intensity of the line (I_T):

$$\frac{dI_N}{d\omega}=\frac{n_p^{-1}\,dI/d\omega}{\int (dI/d\omega)\,d\omega}=\frac{dI/d\omega}{n_p I_T}\ , \tag{1}$$

where $\omega=\lambda^{-1}$ (inverse wavelength). The advantage of this is that the integrated line intensity is dominated by the atomic resonance, and can be adequately approximated by the atomic line intensity I_A. The well-known formula for the atomic emission intensity per unit volume is[13]

$$I_T\simeq I_A=n_A^*\frac{64\pi^4 c}{3}\left(\frac{\nu_A}{c}\right)^4\mu_A^2\ , \tag{2}$$

where n_a^* is the number density of excited atoms, ν_A is the frequency of the atomic resonance line, and μ_A is the corresponding transition dipole moment. Emission in a far wing is due to close collisions between excited and perturbing atoms, and entails a change of one unit in the orbital angular momentum l.[14] If one assumes that the collisional wave functions associated with $l\pm1$ are not too different than that for l (a good approximation in realistic situations), then the differential intensity per unit volume per unit wave number $\omega(=\lambda^{-1})$ is given within the distorted-wave approximation by

$$\frac{dI(\omega,E)}{d\omega}=n_p n_A^* g\frac{1024\pi^5 c^2}{3v_i}\omega^4\sum_l (2l+1)|T^l(\omega,E)|^2\ , \tag{3a}$$

with

$$T^l(\omega,E)=\int_0^\infty \psi_i^l(E,R)\mu_{if}(R)\psi_f^l(E_f,R)\,dR\ , \tag{3b}$$

where n_p is the number density of perturbers, g is the statistical weight of the initial-state potential that correlates to the relevant atomic level, v_i is the speed of initial relative motion of the colliding atoms, $\psi_i^l(E,R)\sim k_i^{-1/2}\times\sin(kR-\frac{1}{2}l\pi+\delta_l)$ is the initial-channel wave function at internuclear separation R, $\psi_f^l(E_f,R)$ is the final-channel wave function, and $\mu_{if}(R)$ is the transition dipole moment coupling the quasimolecular states. (Note that, $E_f=E_i-hc\omega+hc\omega_A$.)

One can make a significant simplication for the normal-

ized intensity by assuming that $\mu_{if}(R)$ is effectively constant over the range of R that contributes to the spectral range of interest. Although the transition dipole moment is expected to be a slowly varying function of R, it is more difficult to compute accurately than internuclear potentials. Stationary-phase methods based on Jeffreys-Wentzel-Kramers-Brillouin wave functions demonstrate that transitions for a given ω are localized about Condon points R_C associated with the same transitional energy, i.e., where $h\nu = V_i(R_C) - V_f(R_C)$. Except in cases of avoided crossings[15] or collision-induced dipole moments,[6] $\mu_{if}(R)$ should be a slowly varying function of R. Thus, the transition dipole moment will generally have nearly the same value at all the transition Condon points for a given photon energy. Since the Condon points are independent of l, the effective dipole moment can be designated as μ_ω. Consequently, $T^l(\omega,E) = \mu_\omega \langle \psi_i^l | \psi_f^l \rangle$. Finally, for the common experimental case of one or two Condon points per ω, a given spectral region will correspond to a continuous, finite interval of R. As long as this is not large, $\mu_{if}(R)$ will not vary appreciably over the interval. This implies that μ_ω can be replaced by a single value $\bar{\mu}_\omega$ over a limited spectral range of ω. This is generally a good approximation for the entire structure of a spectral rainbow satellite feature.

With the assumption $\mu_{if}(R) = \bar{\mu}_\omega$, the expression for the normalized differential intensity becomes

$$\frac{dI_N}{d\omega} = g\frac{16\pi c}{v_i}\left(\frac{\omega}{\omega_A}\right)^4\left(\frac{\bar{\mu}_\omega}{\mu_A}\right)^2 \times \sum_l (2l+1)\int \psi_i^l(E,R)\psi_f^l(E_f,R)\,dR \quad . \tag{4}$$

This expression has units of (length)^4, due to the choice $\omega = \lambda^{-1}$. Of course, the appeal of this equation is the elimination of a variable transition dipole moment. Since $(\bar{\mu}_\omega/\mu_A)$ is expected to be of order unity, Eq. (4) allows one to concentrate on the intermolecular potentials, the most variable input into calculations and upon which structure in the line shape is most dependent. These can be adjusted until satisfactory agreement is obtained between theoretical and experimental line shapes. The uncertainty in the variation of the transitional dipole moment is expected to have a less pronounced effect.

Since no beam experiment has been made for a far-wing line shape, the actual differential intensity is an average over an initial kinetic energy distribution. The single-energy equation is given because the energy distributions in experiments cannot be guaranteed to be totally thermal. However, if the system is in thermal equilibrium and if only the atomic line is pumped, the distribution is just the thermal one of the atomic collisional energies—as long as densities are low enough to preclude significant populating of bound states through three-body collisions. If these conditions are met, then the thermally averaged normalized line shape is

$$(n_p I_T)^{-1}\frac{dI(\omega,T)}{d\omega} = \frac{2\pi}{(\pi k_B T)^{3/2}}\int_0^\infty E^{1/2}\exp(-E/k_B T) \times \frac{dI_N(\omega,E)}{d\omega}\,dE \quad . \tag{5}$$

The corresponding equations for the absorption coefficient α can be obtained by merely replacing I by α in Eqs. (4) and (5), and by then multiplying the right-hand side of Eq. (4) by $(\omega_A/\omega)^3$.

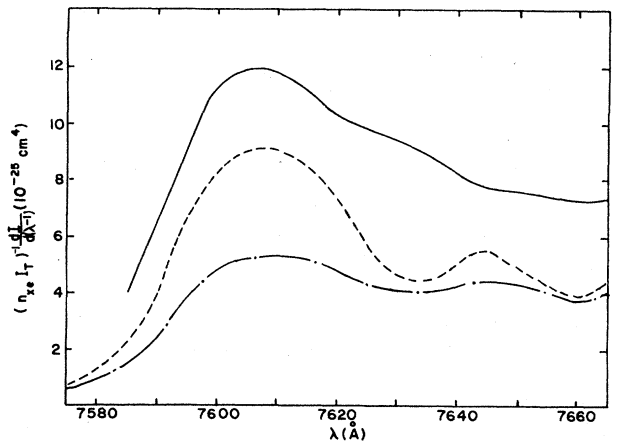

FIG. 1. Normalized differential emission intensities ($\omega = \lambda^{-1}$) for the far blue-wing satellite of the Rb D_2 line (7800 Å) collisionally broadened by Xe perturbers. The solid line (——) is the experimental spectum for a temperature of $T = 706$ K. The simple dashed line (— — —) is a theoretical spectrum at a single incident energy of $\frac{3}{2}k_B T$ [Eq. (4)], while the dash-dot line (— · — · —) is the thermally averaged spectrum [Eq. (5)]. The theoretical spectra are based on the assumption that the local transition dipole moment $\mu_{if}(R)$ is independent of internuclear separation, and is equal to the asymptotic atomic value.

The overlap integral in Eq. (4) can be computed in a variety of ways. An accurate semiclassical method based on an analytic, stationary-phase evaluation of the overlap integral has been reported elsewhere.[11] [Such methods can also handle variations in $\mu_{if}(R)$ to first order about each Condon point.] Figure 1 displays theoretical emission spectra of the satellite feature in the far-blue wing of the Rb D_2 line (7800 Å) of Rb broadened by Xe perturbers, using this stationary-phase technique. ($g = \frac{1}{2}$ instead of $\frac{1}{3}$ because of the large fine-structure splitting.) It has been assumed that $\bar{\mu}_\omega = \mu_A$; in the similar Na-Xe system, the variation of $\mu(R)$ is only about 10% from the atomic value.[16] Figure 1 also displays the experimental results in the low-density (binary collision) limit for a temperature of 706 K.[17] Note that the satellite peak is 200 Å into the blue wing of the atomic line. One of the computed spectra is that for a single incident energy of $\frac{3}{2}k_B T = 0.091$ eV. As discussed in Ref. 11, the potentials were adjusted until the position of the satellite peak and its far-side half-width (i.e., the side opposite the atomic line) roughly matched the experimental values. It was then a joy and relief to see that the normalized intensity agreed acceptably well with experimental values, for there are no other adjustable parameters.

The single-energy line shape is much more structured than the experimental one, although the slight undulations on the near side of the experimental satellite are real. One expects that the pronounced structure in the theoretical line shape would become broadened and perhaps even washed out through thermal averaging. This can be understood in the following way. The satellite feature is caused by interference between pairs of Condon points R_C associated with the same transitional energy, i.e., where $h\nu = \Delta V(R_C)$. The closer ν is to the atomic resonance value (i.e., farther away from the satellite, on the near side), the greater the separa-

tion of these transition points. Since the undulatory structure of the satellite is due largely to interference effects associated with the wave-functional phases at the Condon points, the wide range of energies and angular momenta introduced through thermal averaging should randomize the structure most noticeably on the near side of the satellite. This is indeed what is seen in the thermally averaged theoretical spectrum shown in Fig. 1.

Unfortunately, the intensity of this spectrum is only about 44% of the experimental spectrum. The change from the single-energy case has happened because satellite transitions for collisional energies $E_l \lesssim \frac{5}{6} k_B T$ occur near the classical turning point for $l=0$, often into bound states of the shallow ground-state well. (Reference 18 describes how the amplitudes and phases of the bound-state wave functions were computed.) At these low incident energies, transitions will be into classically accessible regions of the effective lower-state potential only for relatively small values of angular momenta. Thus, the contributions to $dI/d\omega$ from these energies in the thermal distribution are small. In contrast, the contributions from higher energies were truncated by the centrifugal barrier in the entrance channel, as in the case of $E_l = \frac{3}{2} k_B T$. However, since $E_l \lesssim \frac{5}{6} k_B T$ form a significant fraction of the thermal distribution, the intensity of the averaged spectrum is significantly less than that for a single incident energy of $\frac{3}{2} k_B T$.

The discrepancy between the experimental and theoretical results is most likely due to a combination of two causes. First, the intermolecular potentials utilized in the computation were not finely tuned, and are probably in error to some extent. Secondly, the transition dipole moment may have increased from the atomic value at R_C contributing to the satellite (6–$8a_0$). As a test of the first possibility, a thermally averaged theoretical spectrum was computed for $T=413$ K. Its intensity was about 39% of the experimental one. Thus the intensity discrepancy between the experimental and theoretical spectra changes by $(0.44-0.39)/0.44=0.11$ (or 11%) in going from $T=706$ to 413 K. As for the second possibility, we can consider the similar Na-Xe system. In that case, the same assumption that $\bar{\mu}_\omega = \mu_A$ would introduce an error of $(1.1\mu_a/\mu_A)^2 = 1.2$. Both possible sources of error are expected to generate discrepancies of a few tens of percent. This is consistent with the difference between the experimental and thermally averaged computed spectra. However, the discrepancy in line shape can be attributed to errors in the potentials. (As discussed elsewhere,[9] the secondary peak at 7645 Å is not a rainbow interference supernumerary, in contrast to what would generally be assumed in standard theoretical interpretations.)

Of course, there is the possibility that some factor on the order of $\frac{1}{2}$ was incorrectly omitted in the derivation of Eq. (4). However, several internal and external checks were conducted, and no error was discovered. (This included a comparison to close-coupled calculations on the red-wing absorption spectrum of Sr broadened by Ar perturbers.[19,20]) Consequently, Eq. (4), and the semiclassical method used to evaluate it, seem a viable basis from which to analyze the newly available experimental intensities of far-wing line shapes, and to extract information about intermolecular potentials and transition dipole moments.

The author gratefully acknowledges support for this research from the National Science Foundation through Grant No. PHY 8311397.

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