Semiclassical shape of satellite bands: Application to CsAr

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A term representing interference between classical paths is isolated from the previously derived equation for the semiclassical shape of satellite bands. A band shape quantitatively accurate in the adiabatic one-perturber approximation is given by addition of the classical-path contributions to the interference term. Comparison is made to a quantum-mechanical calculation of a satellite band in the red wing of the self-broadened Lyman-α line of hydrogen and to an experimentally observed band in the blue wing of the cesium 8521-Å resonance line perturbed by argon. The problem of inversion to determine a difference potential from the observed band shape is discussed.

I. INTRODUCTION

Intensities in the wings of pressure-broadened spectral lines are usually[1-3] calculated with classical-mechanical methods. The importance of quantum-mechanical effects has not been firmly established. In the adiabatic approximation the quantum-mechanical formalism[3,4] is well understood, but calculations are very time consuming even with modern computers. It is shown here, by comparison to a two-state quantum-mechanical computation, that the major contributions to the line shape from quantum effects are interference between allowed classical paths and intensity from classically forbidden paths. These contributions can be accounted for semiclassically. The shape of the satellite band in the blue wing of the cesium 8521-Å resonance line is investigated with the semiclassical formalism.

In a previous paper[5] the shape of satellite bands was derived in the one-perturber adiabatic approximation. Semiclassical methods were used to include interference between the allowed classical paths and contributions from classically forbidden paths. The difference between the interaction potentials of the active atom with the perturbing atom in the two states involved in the transition was represented by a parabola. The shape of a satellite band in the red wing of the resonance-broadened Lyman-α line was calculated with the semiclassical formula and compared with those calculated with an exact quantum-mechanical equation and with the classical formula in which contributions from the allowed classical paths are simply added. An encouraging agreement in shape between the semiclassical and quantum-mechanical results was found.[5,6] The interference between classical paths removed the singularity in the classical one-perturber spectrum and caused secondary oscillations to appear between the central line and the satellite band. It was observed, however, that the agreement with the quantum-mechanical result in absolute intensity was excellent for the classical spectrum, but only fair for the semiclassical one. This was attributed to the use of the parabolic approximation to the difference potential in deriving the semiclassical formula.

In a classical treatment, the energy of light absorbed or emitted by an active atom a distance r from a perturber is given by the value of the difference potential at that distance. When the difference potential has an extremum there is a frequency range where more than one classical path is allowed and a range where there is no allowed classical path. A semiclassical treatment reveals a characteristic "rainbow effect" with interference structure in the allowed region accompanied by exponentially decaying intensity in the forbidden region. For brevity, we will use the term "interference" to refer to nonclassical contributions in both regions. In a quantum-mechanical treatment the over-all structure arises from the energy dependence of the Franck-Condon overlap factors.

In this paper the semiclassical formula is reexamined and the pure interference contribution is isolated. The interference is important for a limited region of internuclear distance where the parabolic approximation is valid. The classical result that was shown to give good absolute intensities is then added to the interference spectrum to give quantitative agreement with the quantum-mechanical result. Comparison is again made for the satellite of the Lyman-α line. The observed shape of the blue wing of the 8521-Å resonance line of cesium perturbed by argon[7] is analyzed. The spectrum is inverted to find the difference potential between the ground $^2\Sigma$ and the first excited $^2\Sigma$ states of the CsAr diatomic

molecule. The uniqueness of the inversion is discussed. The CsAr spectrum was chosen for analysis because of the availability of high quality absolute intensities measured in absorption at low densities by Chen and Phelps.[7]

II. FORMALISM

In the independent perturber approximation the total line shape can be calculated for any temperature and pressure if the one-perturber spectrum is known.[2,8] The one-perturber spectrum is well represented by the quasistatic approximation to the classical spectrum as long as satellite bands are absent. When the difference potential has an extremum a satellite appears near the frequency corresponding to the extremum. Transitions at frequencies farther from the central line than the satellite are classically forbidden, and those nearer the central line may occur at more than one interatomic distance. At the extremum the classical intensity becomes infinite. Quantum-mechanical interference between the classical paths removes the singularity, contributes an exponentially decreasing intensity beyond the extremum, and causes secondary oscillations between the extremum and the central line. The absorption coefficient in the presence of one perturber α_ν is expressed as the sum of a classical term and an interference term

$$\alpha_\nu = \alpha_\nu^{\text{class}} + \alpha_\nu^{\text{int}}. \tag{1}$$

The quasistatic approximation may be used for the classical term. The dynamic form[5,9,10]

$$\alpha_\nu^{\text{class}}(b \to a) = 8.7856\times 10^{-43} n_b n_p \omega_b \omega D^2(r) r^2 h\nu \left(\frac{d(h\nu)}{dr}\right)^{-1} \int_0^\infty \left[\left(\epsilon - \frac{V_b(r)}{kT}\right)^{1/2} - \left(\epsilon - \frac{V_b(r)}{kT} - \frac{\epsilon b_m^2}{r^2}\right)^{1/2}\right] e^{-\epsilon}\, d\epsilon \tag{2}$$

is used here because it is directly related to the semiclassical formula.[3] In Eq. (2) ω_b and ω are statistical weights, $D(r)$ is the transition dipole, $h\nu$ is the transition energy or difference potential, and $V_b(r)$ is the interaction potential in the initial electronic state. The value of ω is $\frac{1}{2}$ if the perturbing and absorbing atoms are identical; otherwise it is 1. The term b_m is the maximum value of the impact parameter for which penetration to the distance r with energy equal to ϵkT is classically allowed.

The interference term must approach zero when the frequency is far from that of the satellite band and it must exactly cancel the classical singularity. This term is easily extracted from the semiclassical spectrum.

The semiclassical line-shape function [Eq. (51) of Ref. 5] is a continuous function:

$$T^{\pm}(u, T^*) = |u| \int_0^\infty y^{-2}\, \mathrm{Ai}^2(\pm y) \exp\left[-\left(\frac{|u^3|}{y^3} + \frac{\Delta(T^*|u^3|/y^3)}{T^*}\right)\right] dy, \tag{3}$$

where $u = (\mu/\hbar^2 kT\Delta V'')^{1/3} h(\nu_s - \nu)$, the reduced temperature $T^* = kT/-V_b(r_m)$, ΔV is the difference potential, and Δ is a correction for the effects of the centrifugal potential. Ai is the Airy function. The plus branch is used for frequencies farther from the central line than the satellite, and the minus branch is used inside the satellite. The interference contribution to the line shape cannot be continuous because it must cancel the classical singularity at $u = 0$. When $u > 0$ all of the intensity comes from interference; therefore $T^+(u, T^*)$ is the interference term for frequencies outside the satellite. The classical component is given by Eq. (13) with $\mathrm{Ai}^2(-y)$ replaced by $1/2\pi y^{1/2}$. Red and blue satellite bands are distinguished by the sign of $\Delta V''$, which is positive for a minimum in ΔV and negative for a maximum.

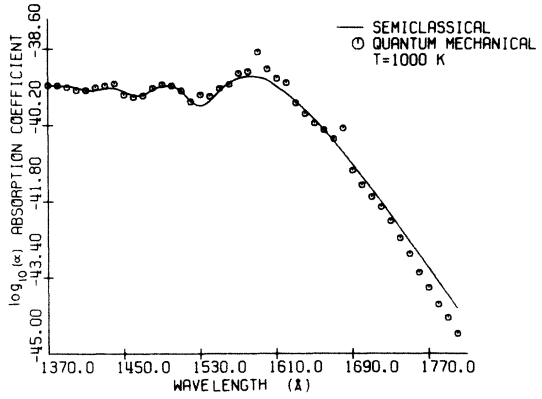

FIG. 1. Comparison of the semiclassical band shape [Eq. (1)] with the quantum-mechanical band shape [Ref. (5)].

The interference contribution to the line shape is then

$$T_{\text{int}}^{+}(u, T^*) = T^+(u, T^*), \tag{4a}$$

$$T_{\text{int}}^{-}(u, T^*) = |u| \int_0^\infty y^{-2}\left[\mathrm{Ai}^2(-y) - \frac{1}{2\pi y^{1/2}}\right] \times \exp\left[-\left(\frac{|u^3|}{y^3} + \frac{(T^*|u^3|/y^3)}{T^*}\right)\right] dy, \tag{4b}$$

and

$$\alpha_\nu^{\rm int} = 6\omega\pi^2 A\nu r_0^2 D^2(r_0)(kT)^{4/3} e^{1/T} \times (\mu/\hbar^2\Delta V'')^{2/3} T_{\rm int}^{\pm}(u, T^*), \quad (5)$$

where

$$A = \frac{64\pi^3 \omega_b n_b n_p h\mu}{3c(2\pi\mu kT)^{3/2}}. \quad (6)$$

The total one-perturber line shape is given by Eqs. (1), (2), and (5).

Much can be learned about the difference potential from an observed spectrum. The interference term is determined by the long-range form of the initial state potential through the function $\Delta(\xi)$ [Eq. (3)], the frequency of the classical satellite ν_s, and the second derivative of the difference potential $\Delta V''$. Values for $\Delta V''$ and ν_s can be deduced from the rate of exponential decrease of the absorption outside the satellite. The interference contribution to the intensity inside the satellite band can then be calculated and subtracted from the observed spectrum to give the classical component. Inversion of the classical component to give a complete $\Delta V(r)$ is complicated by the two classical paths that contribute to the intensity. A unique, direct inversion is impossible. Parameters in a model potential can be determined and a partial direct inversion made.

III. COMPARISON WITH EXACT QUANTUM-MECHANICAL CALCULATION

The semiclassical absorption coefficient given by Eq. (1) was evaluated for the satellite band in the red wing of the resonance broadened Lyman-α line of hydrogen. This system was chosen because an exact quantum-mechanical calculation[5] is available for comparison. The result of that comparison is shown in Fig. 1. The agreement in absolute intensities is quantitative. There is a small amount of "noise" in the quantum-mechanical result that is not matched in the semiclassical spectrum.[6] The noise will diminish for heavier atoms or higher temperatures. There is some remaining discrepancy for wave lengths greater than 1700 Å. This is considered unimportant because the intensity has diminished to a negligible value at those wavelengths.

Two points about the comparison should be emphasized. First, the parameters needed for the semiclassical calculations were taken from the known potential curves. There were no "adjustable" parameters. Second, the accuracy is expected to be better for atoms heavier than hydrogen. The conclusion is that the semiclassical formula [Eq. (1)] is quantitatively accurate for absolute intensities in the wings of atomic lines in the one-perturber adiabatic approximation.

IV. INVERSION

A well-defined inversion procedure has been developed. Knowledge of the initial-state potential is assumed and the difference potential is calculated.

Relative absorption coefficients are divided by the frequency ν to give a line shape J_ν proportional to $T(u, T^*)$,

$$J_\nu = \alpha_\nu/\nu = KT(u, T^*), \quad (7)$$

where u is proportional to $\nu_s - \nu$,

$$u = ah(\nu_s - \nu). \quad (8)$$

An initial-state potential function $V_b(r)$ and an internuclear distance for the classical satellite r_0 are chosen. Then

$$T^* = -kT/V_b(r_0). \quad (9)$$

If $T^* > 5$, the relative line shape is insensitive to T^* and therefore to r_0. A nonlinear least-squares fit of Eq. (7) to values of J_ν in the vicinity of the satellite is made to give values for K, a, and ν_s. The second derivative of the difference potential is determined from

$$\Delta V''(r_0) = \mu/\hbar^2 kTa^3, \quad (10)$$

and the quadratic approximation to the difference potential is

$$\Delta V(r) = h\nu_s + \Delta V''(r_0)(r - r_0)^2/2. \quad (11)$$

The interference contribution to the intensity inside the satellite, $KT_{\rm int}^{-}(ah(\nu_s - \nu), T^*)$, is then calculated [Eq. (4b)] and subtracted from the experimental J_ν values to give the classical component $J_\nu^{\rm class}$.

We write the classical intensity [Eq. (2)] as

$$J_\nu^{\rm class} = \left(\frac{d(h\nu)}{dr}\right)^{-1} J_r^{\rm class}. \quad (12)$$

The constants are adjusted to correspond to the value of K determined from the fit, and $J_r^{\rm class}$, which is independent of the difference potential, is calculated.

This is the point at which the inherent ambiguity in the assignment of intensity to the two classical paths must be faced. In most cases, the large r branch will dominate for frequencies well inside the satellite because the value of the derivative $d(h\nu)/dr$ usually increases rapidly for smaller r. In view of this, a model potential is used from small r out to a distance r_c slightly larger than r_s. The inversion is begun at r_c and continued to larger r. A three-parameter model potential

(such as the quadratic) can be determined directly from the values of r_0, ν_s, and $\Delta V''$. A four-parameter model potential can be determined by the additional imposition of continuity in the derivative of the difference potential at r_c.

The inversion procedure is simple. The contribution to J_ν^{class} from the inner path is subtracted to give $J_\nu^{\text{class, out}}$. Then

$$\frac{d\Delta V}{dr} = \frac{J_r^{\text{class}}}{J_\nu^{\text{class, out}}}. \tag{13}$$

The differential equation is solved by standard numerical techniques such as Runge-Kutta integration.

In the foregoing discussion absolute intensities were not used, but a knowledge of the internuclear distance of the classical satellite r_0 was assumed. The absolute intensity is proportional to $[r_0 D(r_0)]^2$. If the absolute intensity and the transition dipole $D(r_0)$ are both accurately known, r_0 can be determined.

V. APPLICATION TO OBSERVED SPECTRUM

A comparison with a spectrum observed at low pressures is made to test the utility of the formula in interpreting an experimental spectrum. Chen and Phelps have recorded a single tracing of the blue satellite of the Cs 8521-Å resonance line perturbed by argon [Fig. 6 of Ref. 7]. This spectrum was chosen for comparison because absolute intensities are recorded, the spectrum is free of noise, the satellite is well separated from the central line, and there is some evidence of interference structure in the spectrum.

An interaction potential for the initial state was taken from Baylis.[11] The internuclear distance of the maximum in ΔV was estimated from absolute intensities to be $r_0 = 10.6a_0$. The parameters resulting from the least-squares fit are $K = 3.46 \pm 0.06 \times 10^7 a_0^6/e^2$, $a = 3.2 \pm 0.2 \times 10^3 a_0/e^2$, and $h\nu_s = 5.4557 \pm 0.0003 \times 10^{-2} e^2/a_0$.[12] The error limits are statistical and do not include possible systematic errors such as those resulting from inaccuracy in the initial-state potential. From these values $\Delta V''(r_0) = -1.399 \times 10^{-3} e^2/a_0^3$ and the wave length of the classical satellite $\lambda_s = 8351.5$ Å.

A point of interest is that $\lambda_s = 8351.5$ Å, but the maximum intensity in the satellite is at $\lambda = 8367$ Å. It is not a good approximation in this case to assign the extremum in the difference potential to be the frequency of the maximum in the satellite band.

The difference potential resulting from the inversion is shown as the solid line in Fig. 2. The dashed line is the extension of the quadratic potential. The inversion was carried out for wave lengths from 8511 to 8321 Å. The calculated spectrum is shown in Fig. 3. It is indistinguishable on this scale from the observed spectrum.

In the CsAr application the quadratic model potential gave a nearly continuous first derivative at the matching point r_c. This made the use of a four-parameter model potential unnecessary.

The difference potential presented here is in substantial agreement with those of Hedges, Drummond, and Gallagher[13] and Atakan and Jacobsen.[8] The value and curvature at the maximum are similar in each case. The internuclear distance of the maximum is found with our method, but it is subject to uncertainties in the value of the transition dipole and the absolute intensities. We do not regard the difference between the value

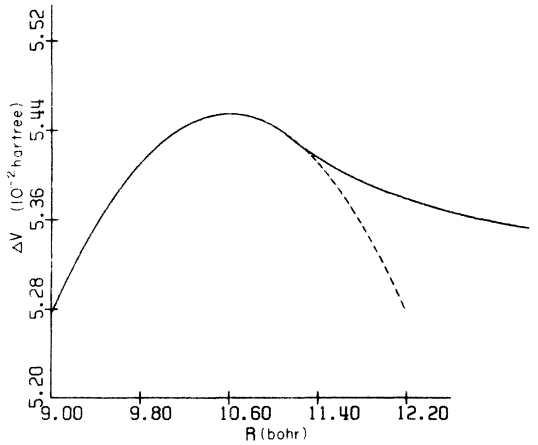

FIG. 2. Difference potential between the ground and first excited $^2\Sigma$ states of CsAr obtained by inversion. The dashed line is an extension of the quadratic that is used for smaller distances.

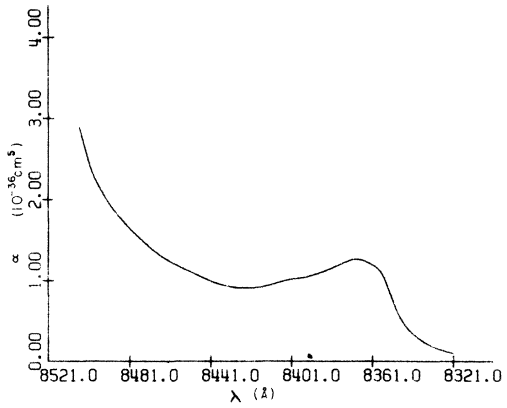

FIG. 3. Blue wing of the CsAr 8521-Å line calculated with Eq. (1). On the scale of the plot the spectrum is indistinguishable from the experimentally observed one [Ref. (7)].

($r_0 = 9.0a_0$) of Hedges, *et al.* and our value ($r_0 = 10.6a_0$) to be significant.

VI. CONCLUSIONS

A quantitatively accurate semiclassical formula for the absolute intensity in the wings of spectral lines has been derived. Satellite bands are treated by adding an interference term to the classical contributions. The formula has been shown to reproduce the results of an exact quantum-mechanical calculation of hydrogen self-broadening. With a reasonable difference potential it also matches the observed intensity in the blue wing of the 8521-Å line of Cs perturbed by argon. Substantial evidence has been obtained that at least some of the satellite bands that have been experimentally observed arise from extrema in difference potentials.

An inversion procedure was developed for determining a difference potential from the shape of a satellite band observed at low densities. The magnitude of the extremum in the difference potential and the second derivative at the extremum are uniquely determined by a least-squares fit to the semiclassical band shape. The internuclear distance of the extremum may also be determined uniquely if the absolute intensity and the value of the transition moment are both accurately known.

There is not enough information in the shape of a satellite band at a single temperature and pressure for a unique inversion to give a complete difference potential.

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