

Semiclassical Shape of Satellite Bands

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When an atom emits or absorbs radiation in the presence of perturbing atoms, satellite bands frequently appear in the spectrum. Such bands may occur when the active atom is subject to equal forces in the two states involved in the transition for some particular configuration of perturbers. In this work a semiclassical approach is used to derive an approximate expression for the one-perturber spectrum in the two-state adiabatic approximation. The expression, which involves an average over Airy functions, is readily adapted for rapid numerical evaluation. Also, an analytic expression for the rate of decline in intensity on the classically forbidden far side of the satellite is found. The semiclassical one-perturber line shape for satellite bands is compared with the classical and quantum-mechanical counterparts for the case of resonance broadening of the Lyman- α line in absorption. The semiclassical line shape is found to be much more realistic than the classical shape in which the satellite appears as a singularity. The semiclassical treatment provides an interpretation of the shape of a satellite band in terms of the intermolecular potentials, a possibility not evident in the exact quantum-mechanical treatment.

I. INTRODUCTION

Satellite bands in the spectra of metal atoms perturbed by foreign gases have been the subject of many investigations, both experimental¹ and theoretical.² The bands, as well as the shift and broadening of the central line, are due to unequal perturbing effects of the foreign gas on the two states of the metal atom involved in the transition. The appearance of satellite bands has most often been attributed³ to the occurrence of equal forces (that is, parallel potential-energy curves) on the metal atom in the two states at some particular configuration of metal atom and foreign gas atoms or molecules.

Although the pressures at which satellite bands are usually observed are too high for the one-perturber line shape to be adequate in itself, it is an important contributor in the wings of a spectral line. A realistic and tractable formula for that shape has not been available. A useful formulation should take cognizance of the fact that most experiments are done with a thermal distribution of translational energies; it should be simple enough so that it is amenable to interpretation, and it should predict a realistic shape.

The most commonly used line shape is the classical one (usually in the quasistatic approximation),²⁻⁴ There are two potential-energy curves required, representing the interaction of the active atom in each of the two states involved in the transition with a perturber atom. The difference between the two potential-energy curves is the difference potential.

The classical line shape for satellite bands is not realistic. The classical line shape has a singularity, the classical satellite, when the differ-

ence potential has an extremum. The intensity is zero outside the classical satellite. This is a direct result of the conservation of momentum in the classical Franck-Condon principle, a condition not necessary in the quantum-mechanical treatment.

The quantum-mechanical one-perturber line shape⁵ is exact, but the formulation is not amenable to interpretation. Furthermore, it is very expensive to compute. There have been only two complete quantum-mechanical calculations⁶ of the shape of a satellite band, one of which will be reported here.

In Sec. II we use a semiclassical approach to derive expressions for the shape of satellite bands for the two-state adiabatic one-perturber case. In Sec. III we introduce a parabolic approximation to the difference potential and perform a thermal average to obtain an equation for the line shape that is realistic and depends explicitly upon parameters characterizing the potential-energy curves. In Sec. IV we compare classical, semiclassical, and quantum-mechanical calculations for a satellite band in the red wing of the resonance-broadened Lyman- α absorption line.

II. SEMICLASSICAL APPROXIMATION

The derivation will be presented for the case of absorption via a parallel transition. Spontaneous and induced emission and nonparallel transitions can be handled similarly. The basic quantum-mechanical expression for the absorption of radiation of frequency ν by a pair of colliding atoms to go to a free state of the electronically excited pair is⁵

$$\alpha_\nu(b \rightarrow a) = A\nu \int dE_b E_a^{-1/2} E_b^{-1/2} e^{-E_b/kT} T_\nu(E_b), \quad (1)$$

with

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

and

$$T_\nu(E_b) = \sum_J \sum_{J'} \omega_J S_{JJ'} |\langle g_b^{K_b, J} | D_{||} | g_a^{K_a, J'} \rangle|^2. \quad (3)$$

Here b represents the initial electronic state and a the final state, E_a and E_b are the energies of nuclear motion in the two states, $K = (2\mu E/\hbar^2)^{1/2}$, ω_b is the statistical weight of state b , n_b and n_p are the number densities of the active atoms in their initial state and of the perturber atoms, respectively, $S_{JJ'}$ is the Hönl-London factor, $D_{||}$ is the dipole-strength function, $g^{K, J}$ is the wave function for nuclear motion, and c , h , μ , k , and T have their usual meanings as the speed of light, Planck's constant, the reduced mass of the pair of colliding atoms, Boltzmann's constant, and the absolute temperature. As a result of the approximations that will be made later, the expressions that are derived are also applicable when the final state is a bound state.

We will concentrate our attention on the function $T_\nu(E_b)$. The first assumption is that the wave number K_b is sufficiently large that many angular-momentum states contribute and the JWKB approximation for the wave functions is appropriate. This assumption will be good for most heavy atoms and for light atoms at high temperatures. It follows that the wave functions for allowed values of J' are approximately equal to $g_a^{K_a, J'}$. Thus,

$$T_\nu(E_b) \cong \sum_J \omega_J \left(\sum_{J'} S_{JJ'} \right) |\langle g_b^{K_b, J} | D_{||} | g_a^{K_a, J'} \rangle|^2 \quad (4)$$

and

$$T_\nu(E_b) \cong \sum_J \omega_J (2J+1) |\langle g_b^{K_b, J} | D_{||} | g_a^{K_a, J} \rangle|^2. \quad (5)$$

Also, ω_J will be replaced by its average value ω ($\frac{1}{2}$ for a homonuclear molecule).

We write $g_b^{K_b, J}$ and $g_a^{K_a, J}$ in the JWKB form

$$g_b^{K_b, J} = [K_b/K_b^J(r)]^{1/2} \sin \left[\int_{r_t}^r K_b^J(r) dr + \delta_b^J \right], \quad (6)$$

$$g_a^{K_a, J} = [K_a/K_a^J(r)]^{1/2} \sin \left[\int_{r_t}^r K_a^J(r) dr + \delta_a^J \right], \quad (7)$$

where

$$K_b^J(r) = [K_b^2 - 2\mu V_b(r)/\hbar^2 - J(J+1)/r^2]^{1/2} \quad (8)$$

and

$$K_a^J(r) = [K_a^2 - 2\mu V_a(r)/\hbar^2 - J(J+1)/r^2]^{1/2}, \quad (9)$$

with $V_b(r)$ and $V_a(r)$ the potential functions in the initial and final state. The function $V_b(r)$ is restricted to be negative in the region of interest to avoid problems near classical turning points. Since we will be concerned only with the variation of the JWKB phase with r and not with its absolute

magnitude, the choice of r_t in Eqs. (6) and (7) is somewhat arbitrary. The effects of a change in the choice of r_t can be considered to be taken up in the values of δ_b^J and δ_a^J which are functions of r_t , as well as J , but still independent of r . A logical choice of r_t is the larger of the two classical inner turning points. We will make the assumption later that the distance at which the transition occurs is far from r_t .

If we now define

$$\begin{aligned} \phi_-^J(r) &= \phi_b^J(r) - \phi_a^J(r) \\ &= \int_{r_t}^r [K_b^J(r) - K_a^J(r)] dr + \delta_b^J - \delta_a^J \end{aligned} \quad (10)$$

and

$$\begin{aligned} \phi_+^J(r) &= \phi_b^J(r) + \phi_a^J(r) \\ &= \int_{r_t}^r [K_b^J(r) + K_a^J(r)] dr + \delta_b^J + \delta_a^J, \end{aligned} \quad (11)$$

then

$$\begin{aligned} g_b^{K_b, J} g_a^{K_a, J} &= \frac{1}{2} [K_b K_a / K_b^J(r) K_a^J(r)]^{1/2} \\ &\times [\cos \phi_-^J(r) - \cos \phi_+^J(r)]. \end{aligned} \quad (12)$$

From Eqs. (5) and (12), we obtain

$$\begin{aligned} T_\nu(E_b) &= \frac{\omega}{4} \sum_J (2J+1) \left[\int_{r_t}^\infty \left(\frac{K_b K_a}{K_b^J(r) K_a^J(r)} \right)^{1/2} \right. \\ &\quad \left. \times D_{||}(r) [\cos \phi_-^J(r) - \cos \phi_+^J(r)] dr \right]^2. \end{aligned} \quad (13)$$

Since $\cos \phi_+^J(r)$ is a rapidly oscillating function of r , it will contribute little to the integral so that

$$\begin{aligned} T_\nu(E_b) &\cong \frac{\omega}{4} \sum_J (2J+1) \left[\int_{r_t}^\infty \left(\frac{K_b K_a}{K_b^J(r) K_a^J(r)} \right)^{1/2} \right. \\ &\quad \left. \times D_{||}(r) \cos \phi_-^J(r) dr \right]^2. \end{aligned} \quad (14)$$

The function $\phi_-^J(r)$ is now expanded in a Taylor series about a point r_0 ,

$$\begin{aligned} \phi_-^J(r) &= \phi_-^J(r_0) + \phi_-^{J'}(r_0)(r-r_0) + \frac{1}{2} \phi_-^{J''}(r_0)(r-r_0)^2 \\ &\quad + \frac{1}{6} \phi_-^{J'''}(r_0)(r-r_0)^3 + \dots \end{aligned} \quad (15)$$

The derivation to this point closely follows that of Jablonski⁷; however, we are interested in contributions to $T_\nu(E_b)$ from internuclear distances r where the potential curves are parallel. The third-derivative term must therefore be retained and the derivation departs from that of Jablonski. We differentiate Eq. (10) to obtain

$$\begin{aligned} \phi_-^{J'}(r_0) &= K_b^J(r_0) - K_a^J(r_0), \\ \phi_-^{J''}(r_0) &= K_b^{J'}(r_0) - K_a^{J'}(r_0), \\ \phi_-^{J'''}(r_0) &= K_b^{J''}(r_0) - K_a^{J''}(r_0). \end{aligned} \quad (16)$$

We choose r_0 to be a point of stationary phase so that r_0 is defined by the equation

$$K_b^J(r_0) = K_a^J(r_0). \quad (17)$$

Equation (17) can be rearranged to give

$$\Delta V(r_0) + h\nu_0 = h\nu, \quad (18)$$

where ν_0 is the frequency of the unperturbed line and the difference potential

$$\Delta V(r) = V_a(r) - V_b(r). \quad (19)$$

Then r_0 , as defined implicitly by Eq. (18), is a function only of the frequency ν . The corresponding expression for ϕ_-^J is

$$\phi_-^J(r) = \alpha + \gamma\xi^2 + \delta\xi^3, \quad (20)$$

where $\xi = r - r_0$. With the cubic term absent this is the form used by Jablonski to derive the semiclassical expression for the classically allowed absorption. With the cubic term added, a simple transformation permits the integral in Eq. (14) to be evaluated as an Airy function.

Two problems now arise: r_0 is, in general, a multivalued function of ν ; Eq. (18) will have complex-valued solutions for frequencies farther from the central line than the satellite. In Sec. III, approximations are introduced that circumvent these difficulties and also lead to accurate formulas for the semiclassical shape of satellite bands which are susceptible to interpretation in terms of the potential energies of interaction between the atoms.

III. APPROXIMATE ANALYTIC EXPRESSIONS

The method described in Sec. II is an accurate interpretation of satellite bands in terms of the JWKB approximation. In this section we will make two additional approximations in order to obtain equations which are easy to evaluate and interpret. We first introduce Eq. (20) into Eq. (14), so that

$$T_\nu(E_b) = \frac{\omega}{4} \sum_J (2J+1) \left[\int_{r_t-r_0}^{\infty} \left(\frac{K_b K_a}{K_b^J(r) K_a^J(r)} \right)^{1/2} \times D_{11}(r) \cos(\alpha + \gamma\xi^2 + \delta\xi^3) d\xi \right]^2. \quad (21)$$

If r_0 is far from r_t , the integration limits can be extended to $-\infty$ and $+\infty$ since for large values of ξ the integrand will alternately become positive and negative and the contributions will largely cancel out. If, in addition, we consider that the dipole-strength function $D_{11}(r)$ and $K_b^J(r)$ and $K_a^J(r)$ are slowly varying functions of r in the vicinity of r_0 , we can write

$$T_\nu(E_b) = \frac{\omega}{4} \sum_J (2J+1) \left(\frac{K_b K_a}{K_b^J(r_0) K_a^J(r_0)} \right) D_{11}^2(r_0) \times \left[\int_{-\infty}^{\infty} \cos(\alpha + \gamma\xi^2 + \delta\xi^3) d\xi \right]^2. \quad (22)$$

The substitution

$$x = \xi + \gamma/3\delta \quad (23)$$

gives

$$T_\nu(E_b) = \frac{\omega}{4} \sum_J (2J+1) \left(\frac{K_b K_a}{K_b^J(r_0) K_a^J(r_0)} \right) D_{11}^2(r_0) \left[\int_{-\infty}^{\infty} \cos \left(\alpha + \frac{2\gamma^3}{27\delta^2} - x \frac{\gamma^2}{3\delta} + x^3 \delta \right) dx \right]^2. \quad (24)$$

We expand the cosine,

$$\cos \left(\alpha + \frac{2\gamma^3}{27\delta^2} - x \frac{\gamma^2}{3\delta} + x^3 \delta \right) = \cos \left(\alpha + \frac{2\gamma^3}{27\delta^2} \right) \cos \left(-x \frac{\gamma^2}{3\delta} + x^3 \delta \right) - \sin \left(\alpha + \frac{2\gamma^3}{27\delta^2} \right) \sin \left(-x \frac{\gamma^2}{3\delta} + x^3 \delta \right), \quad (25)$$

and recognize that the sine function is an odd function of x and thus integrates to zero, so that

$$T_\nu(E_b) = \sum_J (2J+1) \omega \left[K_b K_a D_{11}^2(r_0) \cos^2 \left(\alpha + \frac{2\gamma^3}{27\delta^2} \right) / K_b^J(r_0) K_a^J(r_0) \right] \left[\int_0^{\infty} \cos \left(-\frac{\gamma^2}{3\delta} x + \delta x^3 \right) dx \right]^2. \quad (26)$$

The integral is now in a standard form for the Airy function⁸ (Ai), and we obtain, after converting the summation to an integration,

$$T_\nu(E_b) = \omega \pi^2 K_b K_a \int_0^{J_m} \left[\cos^2 \left(\alpha + \frac{2\gamma^3}{27\delta^2} \right) D_{11}^2(r_0) / (3\delta)^{2/3} K_b^J(r_0) K_a^J(r_0) \right] \text{Ai}^2 \left(- (3\delta)^{-1/3} \frac{\gamma^2}{3\delta} \right) d[J(J+1)], \quad (27)$$

where J_m is the maximum value of J for which penetration to the distance r_0 is possible.⁹

The function α is a rapidly varying function of J , so the random-phase approximation is used to replace the square of the cosine by its average value of $\frac{1}{2}$. We then introduce Eq. (27) into Eq. (1)

to obtain

$$\alpha_\nu(b \rightarrow a) = (A\nu\omega\pi^2\mu/\hbar^2) \int dE_b e^{-E_b/\hbar T} \times \int_0^{J_m} [D_{11}^2(r_0)/K_b^J(r_0) K_a^J(r_0)] (3\delta)^{-2/3} \times \text{Ai}^2[-\gamma^2/(3\delta)^{4/3}] d[J(J+1)]. \quad (28)$$

Now

$$\gamma = \frac{1}{2} [K_b^{J'}(r_0) - K_a^{J'}(r_0)], \quad (29)$$

which simplifies to

$$\gamma = \mu \Delta V'(r_0) / 2K_b^J(r_0) \hbar^2. \quad (30)$$

Also,

$$\delta = \frac{1}{6} [K_b^{J'''}(r_0) - K_a^{J'''}(r_0)], \quad (31)$$

which is expanded to

$$\delta = \frac{\mu \Delta V''(r_0)}{6K_b^J(r_0) \hbar^2} \left[1 - \frac{\Delta V'(r_0)}{K_b^J \Delta V''(r_0)} \right. \\ \left. \times \left(\frac{2J(J+1)}{r_0^3} - \frac{\mu [V_a'(r_0) + V_b'(r_0)]}{\hbar^2} \right) \right]. \quad (32)$$

We now introduce the first approximation in addition to the JWKB and stationary-phase approximations. We neglect the second term within the square brackets in Eq. (32). That is, we assume that

$$\frac{\Delta V'(r_0)}{K_b^J(r_0) \Delta V''(r_0)} \left(\frac{2J(J+1)}{r_0^3} - \frac{\mu [V_a'(r_0) + V_b'(r_0)]}{\hbar^2} \right) \ll 1. \quad (33)$$

This condition should be met whenever the JWKB approximation is valid, except near points of inflection in the difference potential. We must have $V_a'' \neq V_b''$.

It is convenient to define

$$y = - \left(\frac{2\mu}{\hbar^2} \right)^{2/3} [K_b^J(r_0)]^{-2/3} \frac{\Delta V'(r_0)^2}{[2\Delta V''(r_0)]^{4/3}}, \quad (34)$$

so that

$$-\gamma^2 / (3\delta)^{4/3} = y. \quad (35)$$

From Eqs. (8) and (34),

$$\frac{dy}{d[J(J+1)]} = - \frac{y^4 \hbar^4 [2\Delta V''(r_0)]^4}{3(2\mu)^2 r_0^2 [\Delta V'(r_0)]^6}. \quad (36)$$

Combining the preceding equations with Eq. (28), we get the expression

$$\alpha_\nu(b \rightarrow a) = [6\omega\pi^2 A\nu\mu r_0^2 D_0^2(r_0) / \hbar^2]^{1/2} (\Delta V' / \Delta V'')^2 \\ \times \int_0^\infty dE_b e^{-E_b/kT} \int_{y_{\min}}^{y_{\max}} y^{-2} \text{Ai}^2(y) dy, \quad (37)$$

where the integration limits y_{\min} and y_{\max} are obtained by substituting $J=0$ and $J=J_m$ in Eq. (34). This expression is accurate within the limitations of the JWKB approximation and it holds for both the red and violet satellites. However, r_0 is a multivalued (we will assume double-valued) function of ν and analytic continuations are necessary in Eqs. (18) and (34) in order to obtain absorption coefficients for frequencies in the classically for-

bidden region of the spectrum. We overcome these difficulties by the expedient of assuming that the difference potential can be represented by a quadratic. This is the second approximation:

$$\Delta V(r) \cong h(\nu_s - \nu_0) + \frac{1}{2} \Delta V''(r_m) (r - r_m)^2, \quad (38)$$

where r_m represents the position of the extremum in the difference potential and ν_s is the frequency of the classical satellite so that $\Delta V(r_m) = h(\nu_s - \nu_0)$. Then from Eq. (18),

$$\Delta V'^2 / 2\Delta V'' = h(\nu - \nu_s), \quad (39)$$

and from Eq. (34),

$$y = (2\mu/\hbar^2)^{2/3} [K_b^J(r_0)]^{-2/3} (2\Delta V'')^{-1/3} h(\nu_s - \nu). \quad (40)$$

We now assert again that $K_b^J(r)$ is a slowly varying function of r and use

$$K_b^J(r_0) \cong K_b^J(r_m). \quad (41)$$

Then Eqs. (39) and (40) provide the necessary analytic continuation to treat frequencies outside of the classical satellite. That is, $h(\nu_s - \nu)$ may be positive or negative.

If we define

$$I^+(y) = - \int_y^\infty t^{-2} \text{Ai}^2(t) dt, \quad (42)$$

$$I^-(y) = \int_{-\infty}^y t^{-2} \text{Ai}^2(t) dt,$$

then

$$\alpha_\nu^*(b \rightarrow a) = 6\omega\pi^2 A\nu\mu r_0^2 D_0^2(r_0) h(\nu_s - \nu) \hbar^{-2} (\Delta V'')^{-1} \\ \times \int_0^\infty dE_b e^{-E_b/kT} [I^+(y_{\max}) - I^+(y_{\min})]. \quad (43)$$

This expression is accurate within the limitations of the quadratic approximation to the difference potential. The α^+ function is to be used for frequencies farther from the unperturbed line than the classical satellite ν_s , whereas the α^- function is to be used inside the classical satellite. The magnitude of y_{\max} is greater than that of y_{\min} ; however, for frequencies inside the satellite, y is negative so actually $y_{\max} < y_{\min}$. If a fixed energy result is desired the integral can be eliminated and E can be set to a fixed value. For that purpose the functions $I^\pm(y)$ are displayed in Fig. 1 and tabulated in Table I.

The minimum value of y , y_{\min} , corresponds [from Eqs. (40) and (41)] to the maximum value of $K_b^J(r_m)$. For fixed energy E_b that value is achieved when $J=0$. Thus,

$$y_{\min} = \left(\frac{2\mu}{\hbar^2} \right)^{2/3} \left(2\Delta V'' \frac{K_b^2 - 2\mu V_b(r_m)}{\hbar^2} \right)^{-1/3} \\ \times h(\nu_s - \nu) \quad (44)$$

and y_{\min} depends upon the properties of the potential functions only at the point where they are par-

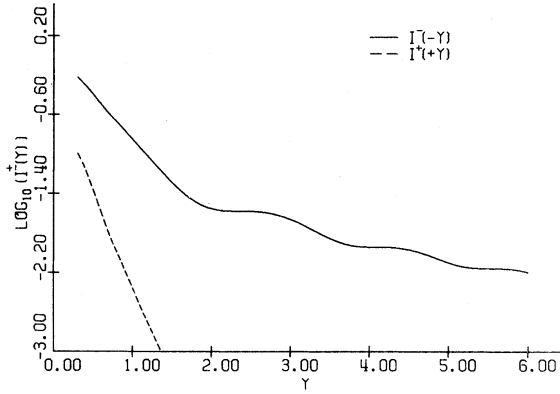


FIG. 1. Functions $I^*(y)$ and $I^(-y)$. They diverge at $y=0$.

allel. The form of y_{\max} is, however, more complicated since it corresponds to the minimum value of $K_b^J(r_m)$. That value is achieved when $J=J_m$, the maximum value of J for which penetration to the distance r_m is possible. The value of y_{\max} will be infinite for energies of collision sufficiently high so that a rotational barrier of that magnitude either does not exist or occurs at a distance smaller than r_m . For lower energies, y_{\max} depends in a complicated and detailed manner upon the longer-range part of the potential $V_b(r)$.

A considerable simplification is achieved by integrating Eq. (43) by parts. We find

$$\alpha_v^{\pm}(b \rightarrow a) = 6\omega\pi^2 A\nu\mu r_0^2 D_{\parallel}^2(r_0) h(\nu_s - \nu) \hbar^{-2} (\Delta V''')^{-1} \times \left[-kT \{ [I^{\pm}(y_{\max}) - I^{\pm}(y_{\min})] e^{-E_b/kT} \}_0^{\infty} + kT \int_0^{\infty} \left(I^{\pm}(y_{\max}) \frac{dy_{\max}}{dE_b} - I^{\pm}(y_{\min}) \frac{dy_{\min}}{dE_b} \right) \times e^{-E_b/kT} dE_b \right]. \quad (45)$$

The first term is zero at the lower limit because

$$y_{\max}(0) = y_{\min}(0) = y(0) \quad (46)$$

and at the upper limit because of the exponential factor. Now y_{\max} is a nondecreasing function of the energy and y_{\min} is a monotonically decreasing function of the energy E_b . Therefore, the second term within the square brackets in Eq. (45) can be rewritten as

$$kT \left[\int_{y(0)}^{\infty} I^{\pm}(y) e^{-E_b/kT} dy + \int_0^{y(0)} I^{\pm}(y) e^{-E_b/kT} dy \right]. \quad (47)$$

The energy E_b is a function of y , but it does not have the same functional form in the two terms in Eq. (47) since in the first term the integration variable stands for the variable y_{\max} and in the second y_{\min} . However, if we consider E_b to be a function of y over the domain $0 < y < \infty$ it is a continuous func-

tion with $E_b(y(0))=0$. We can therefore combine the two terms in Eq. (47) into a single integral with a range of integration between 0 and ∞ . We do this and reexpress the function $E_b(y)$ in a convenient form to achieve the final result, which is suitable for numerical evaluation:

$$\alpha_v^{\pm}(b \rightarrow a) = 6\omega\pi^2 A\nu r_0^2 D_{\parallel}^2(r_0) (kT)^{4/3} e^{1/T^*} \times (\mu/\hbar^2 \Delta V''')^{2/3} T^{\pm}(u, T^*), \quad (48)$$

where

$$u = (\mu/\hbar^2 kT \Delta V''')^{1/3} h(\nu_s - \nu), \quad (49)$$

the reduced temperature

$$T^* = kT / -V_b(r_m), \quad (50)$$

and the line-shape function

$$T^{\pm}(u, T^*) = |u| \int_0^{\infty} y^{-2} \text{Ai}^2(\pm y) \times \exp\{-[|u^3|/y^3 + \Delta(T^*|u^3|/y^3)/T^*]\} dy. \quad (51)$$

The function $\Delta(\xi)$ does not have the same form throughout the region of integration, though it is a continuous function:

$$\Delta(\xi) = \begin{cases} 0, & 1 \leq \xi < \infty \\ \Delta_+(\xi), & 0 \leq \xi < 1. \end{cases} \quad (52)$$

The value of $\Delta_+(\xi)$ depends on the potential at longer range than r_m and must be written implicitly.

We write

$$E_+(\xi) = V_b(r_m) (1 - \xi) + \hbar^2 J_m(J_m + 1)/2\mu r_m^2, \quad (53)$$

where J_m , the maximum value of J for which penetration to the distance r_m with the energy of collision equal to E_+ , is obviously a function of $E_+(\xi)$. Then

$$\Delta_+(\xi) = \hbar^2 J_m(J_m + 1)/2\mu [-V_b(r_m)] r_m^2, \quad (54)$$

so that

$$E_+(\xi) = V_b(r_m) [1 - \xi - \Delta_+(\xi)]. \quad (55)$$

TABLE I. Function $I^{\pm}(y)$. (The power of ten is indicated in parentheses.)

| y | $I^{(+y)}$ | $I^{(-y)}$ |
|-----|------------|------------|
| 0.5 | 4.3435(-2) | 4.0324(-1) |
| 1.0 | 4.3895(-3) | 1.4119(-1) |
| 1.5 | 5.6425(-4) | 5.1585(-2) |
| 2.0 | 7.4797(-5) | 2.7942(-2) |
| 2.5 | 8.6697(-6) | 2.6481(-2) |
| 3.0 | 1.1993(-6) | 2.1820(-2) |
| 3.5 | | 1.3994(-2) |
| 4.0 | | 1.1498(-2) |
| 4.5 | | 1.0794(-2) |
| 5.0 | | 7.9959(-3) |
| 5.5 | | 7.0015(-3) |
| 6.0 | | 6.3647(-3) |

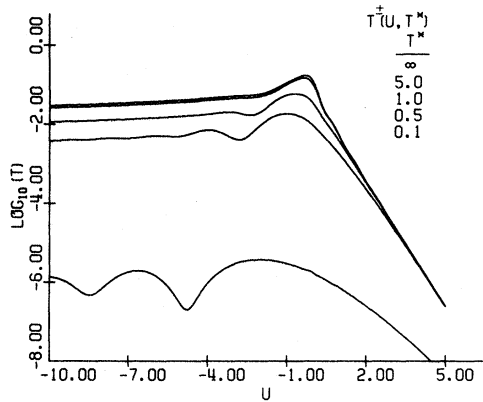


FIG. 2. Function $T^+(u, T^*)$ plotted vs u for several reduced temperatures. The potential used is an attractive r^{-6} potential of arbitrary strength. The $T^* = \infty$ curve is independent of the potential chosen.

The spectrum associated with the satellite (at this level of approximation) is independent of the short-range part of the potential.

The evaluation of $\Delta_+(\xi)$ is the primary obstacle to determining the shape of the spectrum, so although when the potential is known it is a simple matter to evaluate $\Delta_+(\xi)$ numerically, it is tempting to try further approximations which may cause knowledge of the potential to be unnecessary. There are two possibilities which will be discussed here.

(i) Often only the long-range form of the potential is known. If the potential for $r > r_m$ is assumed to be an inverse power potential, the essential features of the spectrum will be retained and the method will be applicable to many actual circumstances. We assume

$$V_b(r) = -c_n/r^n. \tag{56}$$

The effective potential including the centrifugal repulsion is then

$$U(r) = -c_n/r^n + J(J+1)\hbar^2/2\mu r^2. \tag{57}$$

If $n > 2$, $U(r)$ has a maximum at r for a value of J , J_m , such that

$$\hbar^2 J_m(J_m + 1)/2\mu = nc_n/2r^{n-2}. \tag{58}$$

Then from Eq. (54),

$$\Delta_+(\xi) = n/2R^{n-2}, \tag{59}$$

where $R = r/r_m$. The height of the maximum in $U(r)$ is $E_+(\xi)$, so

$$E_+(\xi) = (n-2)c_n/2r^n. \tag{60}$$

Then from Eq. (55),

$$\xi = 1 + (n-2)/2R^n - n/2R^{n-2}. \tag{61}$$

Equations (59) and (61) give $\Delta_+(\xi)$ parametrically in R . Thus $\Delta_+(\xi)$ depends only on the form of the

potential, not on the strength; that is, it depends on n , but not on c_n .

(ii) For high reduced temperatures, $T^* \gg 1$, the value of $\Delta_+(\xi)$ will not affect the answer and all approximations will be unimportant. The infinite temperature limit is also asymptotically correct at finite temperatures for frequencies well outside the classical satellite, $u \gg 1$, since in that case the contributions to the integral from the interval $0 \leq \xi < 1$ will be small due to the increase in the magnitude of the argument of the Airy function. The limit is

$$T^\pm(u, \infty) = |u| \int_0^\infty y^{-2} \text{Ai}^2(\pm y) e^{(-|u^3|/y^3)} dy. \tag{62}$$

The function $T^\pm(u, T^*)$ is displayed in Fig. 2 for several reduced temperatures for the special case of a long-range inverse-sixth-power potential. The infinite temperature limit $T^\pm(u, \infty)$ is a universal function independent of the system and, as such, is tabulated in Table II.

The magnitude of the absorption on the far side of the satellite is expected to decay exponentially. It is of interest to determine analytically the rate of that decay in the limit that the frequency is far from the satellite. We do this by assuming the asymptotic form of the Airy function for large positive arguments so that

$$\text{Ai}^2(y) \approx \frac{1}{4} \pi^{-1} y^{-1/2} e^{-4y^{3/2}/3}. \tag{63}$$

TABLE II. Function $T^\pm(u, \infty)$. (The power of ten is indicated in parentheses.)

| u | $T^+(u, \infty)$ | $T^-(u, \infty)$ |
|------|------------------|------------------|
| 0.2 | 4.742(-2) | 1.708(-1) |
| 0.6 | 1.399(-2) | 1.619(-1) |
| 1.0 | 4.677(-3) | 1.205(-1) |
| 1.4 | 1.644(-3) | 8.579(-2) |
| 1.8 | 5.939(-4) | 6.618(-2) |
| 2.2 | 2.184(-4) | 5.793(-2) |
| 2.6 | 8.135(-5) | 5.505(-2) |
| 3.0 | 3.057(-5) | 5.341(-2) |
| 3.4 | 1.157(-5) | 5.137(-2) |
| 3.8 | 4.405(-6) | 4.883(-2) |
| 4.2 | 1.685(-6) | 4.622(-2) |
| 4.6 | 6.466(-7) | 4.389(-2) |
| 5.0 | 2.490(-7) | 4.196(-2) |
| 5.4 | 9.617(-8) | 4.036(-2) |
| 5.8 | | 3.898(-2) |
| 6.2 | | 3.774(-2) |
| 6.6 | | 3.660(-2) |
| 7.0 | | 3.555(-2) |
| 7.4 | | 3.457(-2) |
| 7.8 | | 3.366(-2) |
| 8.2 | | 3.283(-2) |
| 8.6 | | 3.206(-2) |
| 9.0 | | 3.134(-2) |
| 9.4 | | 3.067(-2) |
| 9.8 | | 3.004(-2) |
| 10.2 | | 2.944(-2) |

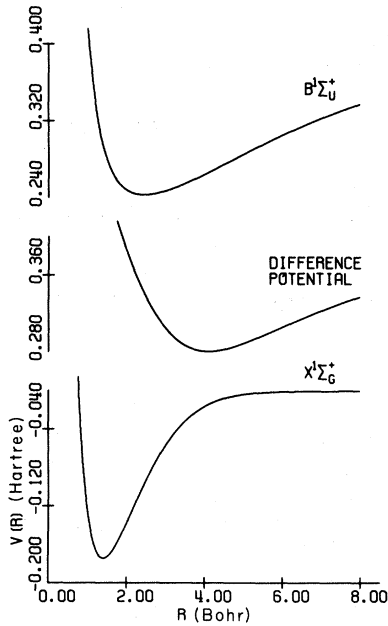


FIG. 3. Potential curves for the X and B states of the hydrogen molecule with their corresponding difference potential.

Then after a change of integration variable,

$$T^+(u, \infty) \cong (u/6\pi) \int_0^\infty e^{-(4/3\pi + u^3 z^2)} dz. \quad (64)$$

The integrand is a sharply peaked function with the maximum occurring when the negative of the argument of the exponential is a minimum. It is thus appropriate to expand the magnitude of the argument about its minimum value,

$$A(z) \cong (12)^{1/3} u + 3u^3 [z - (\frac{2}{3})^{1/3}/u]^2, \quad (65)$$

so that

$$T^+(u, \infty) \cong (u/6\pi) e^{-12^{1/3}u} \times \int_0^\infty \exp\{-3u^3 [z - (\frac{2}{3})^{1/3}/u]^2\} dz. \quad (66)$$

The width of the Gaussian factor decreases faster than the origin ($u^{-3/2}$ vs u^{-1}) for large u , so we extend the lower limit on the integral to $-\infty$. Then

$$T^+(u, \infty) \cong (108\pi)^{-1/2} u^{-1/2} e^{-12^{1/3}u}. \quad (67)$$

Equation (67) should be useful as an analytic expression for the absorbance far in the wings of an atomic line past the satellite band.

IV. COMPARISON OF CLASSICAL, SEMICLASSICAL, AND QUANTUM-MECHANICAL CALCULATIONS OF SATELLITE BAND IN RED WING OF RESONANCE-BROADENED LYMAN- α

There are many contributions to the resonance broadening of the Lyman- α line corresponding to transitions from free states of nuclear motion in

either the singlet or triplet molecular electronic states representing the interaction of ground-state atoms to one of the family of molecular states representing the interaction of 2^2P atoms with ground-state atoms. These contributions are additive in the Born-Oppenheimer approximation with appropriate statistical weights. This study is restricted to transitions from the $X^1\Sigma_g^+$ state to the $B^1\Sigma_u^+$ state, the process by which broadening farthest to the red is possible.⁴

The two potential-energy curves and the difference potential are shown in Fig. 3. The difference potential has a minimum at a separation of 4.1 bohr and energy corresponding to a wavelength of 1623 Å. The result is that absorption at wavelengths greater than 1623 Å is classically forbidden. It is of considerable importance for stellar atmosphere calculations¹⁰ to determine accurately the rate of decrease of the absorption toward the red from 1623 Å. The quantum-mechanical calculation gives a numerical result and the semiclassical treatment gives, in addition, an analytical expression for the rate of decrease of absorption.

The potential curves used in the calculations to be described are those given by Kolos and Wolniewicz.¹¹ The dipole-strength function for the $X \rightarrow B$ transition is that determined by Browne.¹²

A. Classical Formulation

The classical result for this system has been reported for one temperature.⁴ The formula to be evaluated is^{7,9}

$$\alpha_\nu(b \rightarrow a) = 4.3928 \times 10^{-43} n_b n_p \omega_b D^2(r) r^2 \times h\nu \left(\frac{d(h\nu)}{dr}\right)^{-1} \int_0^\infty \left[\left(\epsilon - \frac{V_b(r)}{kT}\right)^{1/2} - \left(\epsilon - \frac{V_b(r)}{kT} - \frac{\epsilon b_m^2}{r^2}\right)^{1/2}\right] e^{-\epsilon} d\epsilon. \quad (68)$$

Here n_b and n_p are the number densities of the active atoms in their initial state and of the perturber atoms, respectively, ω_b is the statistical weight of the initial electronic state, $D(r)$ is the dipole-strength function for the transition, $h\nu$ is the transition energy, r is the internuclear distance at which the transition occurs, $V_b(r)$ is the initial-state potential, and b_m is a complicated function of ϵ and r representing the maximum value of the impact parameter for which penetration to the distance r is possible with the energy of collision equal to ϵkT . If all quantities on the right-hand side are in atomic units, α_ν will be in units of cm^5 . The energy integration was done numerically using Laguerre-Gauss integration.

The classical, semiclassical, and quantum-mechanical results are compared in Figs. 4-6 for three different temperatures. The classical ab-

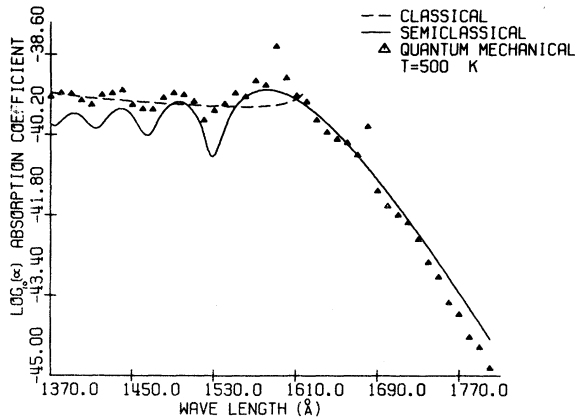


FIG. 4. Comparison of the classical, semiclassical, and quantum-mechanical one-perturber line shapes for the satellite band at a temperature of 500 K. The classical absorption coefficient has a singularity at $\lambda = 1623 \text{ \AA}$ corresponding to the minimum in the difference potential of Fig. 3.

sorption coefficient diverges at $\lambda = 1623 \text{ \AA}$, exhibits no oscillations for wavelengths less than 1623 \AA , and is zero to the red of the satellite. The absolute intensity is accurate, however, and appears to bisect the quantum oscillations. The integrated absorption should be useful for total cross-section determinations.¹³

B. Quantum-Mechanical Formulation

In the quantum-mechanical formulation the process is one of free-bound absorption. For any reasonable temperature the free-free contribution to the quasimolecular absorption from the X to the B state is negligible except for wavelengths near that of the atomic line. The basic formula is [Eq. (10) of Ref. 5(a)]

$$\alpha_{\nu}(b \rightarrow a) = \omega_b \frac{16\pi^3 \nu}{3hc} n_b n_p \frac{\hbar^3 (2\mu)^{1/2}}{(2\pi\mu kT)^{3/2}} \times \sum_{\nu} \sum_{J'} \sum_J S_{JJ'} E_b^{-1/2} e^{-E_b/kT} \omega_{J'} \times |\langle g_b^{K,J} | D | g_a^{\nu',J'} \rangle|^2, \quad (69)$$

where E_b is the initial-state energy of nuclear motion, $\omega_{J'}$ is the rotational weight, $S_{JJ'}$ is the Hönl-London factor, $K = (2\mu E_b/\hbar^2)^{1/2}$, and $g_b^{K,J}$ and $g_a^{\nu',J'}$ are the continuum and bound wave functions for nuclear motion.

In performing the calculation we were primarily concerned with the long-wave-length portion of the spectrum and temperatures near 5000 K. A total of 66 partial waves were used for transitions to low-lying vibrational levels and levels up through $\nu = 26$ were considered out of a total of approximately 40. The results are not accurate near the atomic line due to the neglect of high vibrational

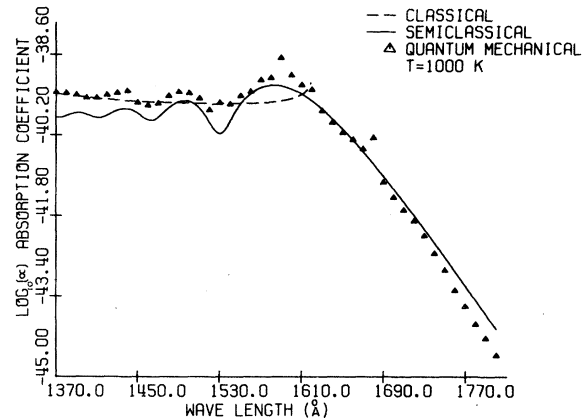


FIG. 5. Comparison of the classical, semiclassical, and quantum-mechanical one-perturber line shapes for the satellite band at a temperature of 1000 K.

levels and the continuum in the upper state.

The wave functions were determined using Numerov integration and the matrix elements were then evaluated using Simpson's rule. Within the limits of numerical accuracy in evaluating the integrals the result represents a lower bound to the total absorption coefficient since it arises from an incomplete sum of positive contributions. A similar straightforward computation for a system such as Cs-Ar would require many more partial waves and would be unfeasible without additional numerical approximations, such as interpolation over partial-wave contributions.

The quantum-mechanical result for Lyman- α resonance broadening provides a good benchmark for assessing the merits of proposed approximate treatments. The absolute intensities in the region $\lambda > 1400 \text{ \AA}$ for $T \leq 5000 \text{ K}$ should be accurate to

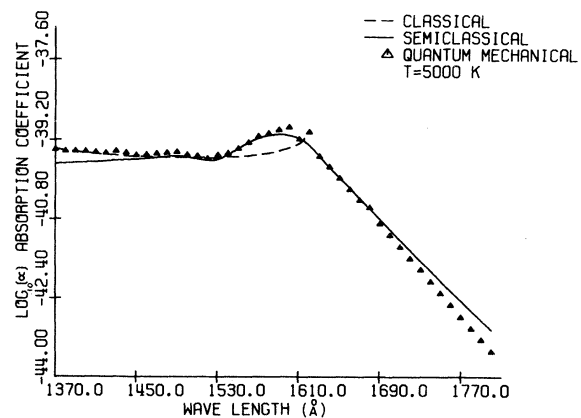


FIG. 6. Comparison of the classical, semiclassical, and quantum-mechanical one-perturber line shapes for the satellite band at a temperature of 5000 K.

within 10%, and thus represent an accurately determined spectrum for a satellite appearing in the red wing of a collisionally broadened line under conditions in which the one-perturber approximation is valid. The results are shown in Figs. 4-6.

The satellite band is found to be quite broad (width ~ 80 Å), there are quantum oscillations on the near side of the satellite, and the absorption falls off exponentially on the far side.

C. Semiclassical Formulation

The semiclassical formulas were derived with the expectation that they will prove to be sufficiently accurate and easy to apply to provide a useful tool in investigating satellite bands in the spectra of metal atoms perturbed by rare gases. The availability of an accurate quantum-mechanical spectrum for the resonance broadening of the Lyman- α line affords an excellent opportunity to test the validity of the semiclassical approach by direct comparison with an exact result. The formula is given by Eq. (48). The derivations in Secs. II and III were performed for the case of free-free absorption; however, the stationary-phase integration is applicable to free-bound transitions as well. Therefore, Eq. (48) is applicable to the resonance broadening of the Lyman- α line even though the spectrum is dominated by free-bound transitions. The computation is discussed briefly in the Appendix.

The spectrum is compared with the quantum-mechanical and classical results in Figs. 4-6. The shapes of the semiclassical and quantum-mechanical spectra are in excellent agreement. The oscillations occur at about the same positions with similar amplitudes. The exponential decrease of absorption outside the satellite is roughly parallel to the quantum-mechanical curve. The deviation of the absolute absorption coefficient from the quantum-mechanical one increases with increasing distance from the satellite. The agreement is excellent near the center of the satellite, but the semiclassical spectrum is lower inside the satellite and higher outside. The probable reason for this is the quadratic approximation to the difference potential.

The $X^1\Sigma_g^+ \rightarrow B^1\Sigma_u^+$ quasimolecular transition is the most important contributor to the absorption spectrum far in the red wing of the Lyman- α line. The absorption decreases exponentially on the red side of the satellite band ($\lambda > 1623$ Å). Equation (67) is evaluated to give an analytic expression for that absorption when $\lambda \gg 1623$ Å. The result is

$$\alpha_\nu(b-a) = 3.916 \times 10^{-38} e^{4492/T} \lambda^{-1} \times \left(0.280808 - \frac{455.6335}{\lambda} \right)^{-1/2}$$

$$\times \exp \left[-\frac{4960}{T^{1/3}} \left(0.280808 - \frac{455.6335}{\lambda} \right) \right]. \quad (70)$$

The formula shows the correct qualitative behavior with temperature and frequency. It predicts an exponential decrease in absorption with frequency with the rate of that decrease inversely proportional to the cube root of the temperature. A least-squares fit of the quantum-mechanical coefficients to the form of Eq. (67) was made to compare with the factor $4960/T^{1/3}$, which is dominant in the rate of decrease of absorption. The best case is that of $T = 1000$ K with the fit comprising wavelengths between 1800 and 2000 Å. The semiclassically predicted exponent, 496, was 20% too low. At some temperatures the exponent was as much as 30% lower than the fitted value. The discrepancy is probably due to the quadratic approximation to the difference potential that was made in Sec. III.

V. CONCLUSIONS

We have applied the semiclassical theory to derive relatively simple expressions for the shape of satellite bands. The basic result is the formula of Eq. (48). Various approximations can be introduced by modifying the function $\Delta(\zeta)$. One of these gives the correct asymptotic intensity outside the satellite [Eq. (67)]. Another type of approximation is to replace the average over initial energies by a single collision energy, say $E = kT$. This approximation is most easily introduced into Eq. (43).

We have demonstrated that the semiclassical formula represents the shape of satellite bands quite well at a minimum of computational effort. The computation time per frequency for one temperature for the quantum-mechanical result was approximately $4\frac{1}{2}$ min on a CDC 6400 computer; for the semiclassical result it was 2 sec and for the classical result 25 msec on an IBM 360/65 computer. The quantum-mechanical computation was done in such a way that the spectrum was evaluated at many temperatures for little additional cost; however, there is still a great difference in difficulty between the methods. This difference will increase in going to heavier atoms such as alkali-metal and rare-gas atoms.

The semiclassical line shape when coupled to an appropriate method for handling many perturber interactions should serve as a very useful tool in investigating satellite bands.

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APPENDIX: COMPUTATION OF SEMICLASSICAL SPECTRUM

The computation involves determining $\Delta(\zeta)$ and then $T^+(u, T^*)$. The absorption coefficient is then obtained by simply multiplying $T^+(u, T^*)$ by the factors appearing in Eq. (48).

A. Computation of $\Delta(\zeta)$

The value of $\Delta(\zeta)$ is zero for $\zeta \geq 1$. For $0 \leq \zeta < 1$, $\Delta(\zeta) = \Delta_+(\zeta)$. A grid of r values starting at r_m is chosen. For each value of r the value of J which will give a barrier maximum at that distance, J_m , and the corresponding barrier height E_+ are found. Then

$$\zeta = 1 - \left(E_+ - \frac{\hbar^2 J_m (J_m + 1)}{2\mu r_m^2} \right) V_b^{-1}(r_m) \quad (71)$$

and

$$\Delta_+ = - \frac{\hbar^2 J_m (J_m + 1)}{2\mu r_m^2 V_b(r_m)} \quad (72)$$

The result is a table of values of ζ vs Δ_+ . We then interpolate on this table to get $\Delta_+(\zeta)$.

B. Computation of $T^+(u, T^*)$ [Eq. (51)]

An integration grid in y is chosen. When u is positive, the integration is straightforward, since the integrand vanishes rapidly for large y . Simpson's-rule integration is used. When u is negative the integrand vanishes as $y^{-5/2}$ when y is large, which is not fast enough for rapid convergence. For large y , the Airy function oscillates about $(2\pi)^{-1} y^{-1/2}$, so this contribution is subtracted out and the remaining integrand is integrated by an averaging technique. The nonoscillating contribution that was subtracted out is then done analytically in case $T^* = \infty$ and corrections to it are evaluated by Legendre-Gauss integration when $T^* < \infty$. The $u=0$ case is a special one. $T(0, \infty)$ can be evaluated analytically. A separate integration is required when $T^* < \infty$.

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¹S. Y. Ch'en *et al.*, *Rev. Mod. Phys.* **29**, 20 (1957); *Physica (Utr.)* **27**, 497 (1961); *J. Quant. Spectrosc. Radiat. Transfer* **4**, 323 (1964); *Phys. Rev.* **188**, 40 (1969).

²M. Takeo, *Phys. Rev. A* **1**, 1143 (1970); A. Royer, *Phys. Rev. A* **4**, 499 (1971), and references therein.

³J. Kieffer, *J. Chem. Phys.* **51**, 1852 (1969); W. R. Hindmarsh and J. M. Farr, *J. Phys. B* **2**, 1388 (1969); J. F. Kielkopf *et al.*, *J. Chem. Phys.* **48**, 5570 (1968); *J. Chem. Phys.* **53**, 2605 (1970).

⁴K. Sando, R. O. Doyle, and A. Dalgarno, *Astrophys. J.* **157**, L143 (1969).

⁵(a)K. M. Sando and A. Dalgarno, *Mol. Phys.* **20**, 103 (1971). (b)R. O. Doyle, *J. Quant. Spectrosc. Radiat. Transfer*

8, 1555 (1968).

⁶A. Royer (private communication) has recently completed a quantum-mechanical calculation.

⁷A. Jablonski, *Phys. Rev.* **68**, 78 (1945).

⁸*Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (U. S. GPO, Washington, D.C., 1964), *Appl. Math. Ser.* **55**, p. 447.

⁹D. R. Bates, *Mon. Not. R. Astron. Soc.* **111**, 303 (1951).

¹⁰O. Gingerich, *Sol. Phys.* **18**, 347 (1971).

¹¹W. Kolos and L. Wolniewicz, *J. Chem. Phys.* **43**, 2429 (1965); *J. Chem. Phys.* **45**, 509 (1966).

¹²J. C. Browne, *Astrophys. J.* **156**, 397 (1969).

¹³D. C. Allison, J. C. Browne, and A. Dalgarno, *Proc. Phys. Soc. Lond.* **89**, 41 (1966).