Exponentially decreasing collision-broadened line shapes

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We obtain asymptotic approximations to the collision-broadened line shape by the method of steepest descent. Exponentially decreasing line shapes result when the phase at the saddle point has an imaginary part. Averaging over a thermal distribution of velocities is shown to substantially affect the line shape.

INTRODUCTION

Exponentially decreasing line shapes are often encountered in the far wing spectra of collision-broadened lines. Satellites,[1,2] for example, have an exponentially decreasing side, and in systems where the difference of the excited and ground-state molecular potentials increases (or decreases) monotonically, one side of the collision broadened line falls off exponentially.[2] This has been referred to as the antistatic wing[2] as opposed to the quasistatic wing[2,3] of the line. In this report we derive expressions for antistatic regions of the line shape by direct asymptotic evaluation of the adiabatic phase-shift expression for the line wing profile.[4,5] The importance of averaging over the thermal distribution of relative velocities is explicitly demonstrated.

THEORY

We consider an isolated optical transition between two nondegenerate levels and neglect nonadiabatic effects (inelastic collisions, quenching, etc.). When the binary-collision approximation is valid (time between collisions long compared to a collision duration), the absorption profile for the line wings may be written

$$I(\Delta)=\frac{1}{2\pi}\frac{\gamma_N+\gamma_c(\Delta)}{\Delta^2}\ , \quad |\Delta| >> \gamma_N+\gamma_c(0)\ , \tag{1}$$

where γ_N is the decay rate due to spontaneous emission, $\Delta=\omega-\omega_0$ is the detuning from resonance, and the collision effects are incorporated in the *detuning dependent* broadening rate $\gamma_c(\Delta)$.[5] The condition $|\Delta| >> \gamma_N+\gamma_c(0)$ ensures that at most a single collision occurs in the time of interest $\tau\sim 1/|\Delta|$, i.e., the interaction of the atom with a single perturber determines the line wing profile.[6] Using classical straight-line trajectories the broadening rate $\gamma_c(\Delta)$ is[5]

$$\gamma_c(\Delta)=n_p v \int_0^\infty 2\pi b\, db \left| \int_{-\infty}^{\infty} dt \frac{V_d[R(t)]}{\hbar} \exp\left[i \left(\Delta t - \int_{-\infty}^{t} dt' \frac{V_d[R(t')]}{\hbar} \right) \right] \right|^2 , \tag{2}$$

where n_p is the perturber density, v is the relative velocity, $V_d(R)$ is the difference between the excited-state and ground-state potentials $V_d(R) = V_e(R)-V_g(R)$, and for straight trajectories $R(t) = (b^2+v^2t^2)^{1/2}$. Equations (1) and (2) are identical to the Anderson theory[4] in the low-density limit and for $|\Delta| >> \gamma_N+\gamma_c(0)$.

The detuning dependence of the broadening rate $\gamma_c(\Delta)$ is governed by the dimensionless parameter $|\Delta| T_d$, where T_d is a characteristic collision duration ($T_d\sim 10^{-12}$ s). Direct asymptotic expansion of Eq. (2) for large $|\Delta| T_d$ may be obtained by the method of steepest descent.[7] In the time integral in Eq. (2), t is allowed to be complex and the main contribution to the integral comes from regions near the saddle points of the exponent $i\phi(t)$ where

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$$\phi(t)=\Delta t-\int_{-\infty}^{t}dt'\frac{V_d[R(t')]}{\hbar}\ . \tag{3}$$

The saddle points are located by $\dot{\phi}(t_s) = 0$ which implies

$$\hbar\Delta=V_d(R_s)\ ;\ \ t_s=\pm\frac{R_s}{v}(1-b^2/R_s^2)^{1/2}\ . \tag{4}$$

The leading order asymptotic approximation to the integral is

$$\int_{-\infty}^{\infty}dt\frac{V_d[R(t)]}{\hbar}e^{i\phi(t)}\simeq\sum_{t_s}\frac{V_d(R_s)}{\hbar}e^{i[\phi(t_s)+\theta_s]}\times\left[\frac{2\pi}{|\ddot{\phi}(t_s)|}\right]^{1/2}, \tag{5}$$

where the sum over t_s includes all saddle points given by Eq. (4) for which $\mathrm{Im}[\phi(t_s)]\geq 0$. The real angle θ_s is chosen so that the integration path is the one of steepest descent and we have assumed $|\ddot{\phi}(t_s)|\neq 0$:

$$|\ddot{\phi}(t_s)|=v\frac{|V_d'(R_s)|}{\hbar}|(1-b^2/R_s^2)|^{1/2}\ .$$

In taking the absolute value squared of Eq. (5), the cross terms involve phase differences $\exp\{i[\mathrm{Re}\phi(t_1)-\mathrm{Re}\phi(t_2)]\}$, where t_1 and t_2 are different saddle points. When the saddle points are well separated these cross terms oscillate rapidly with impact parameter and hence contribute little to the broadening rate.[8] Using these results Eq. (2) becomes

$$\gamma_c(\Delta)=n_p\sum_{t_s}\frac{4\pi^2\Delta^2\hbar}{|V_d'(R_s)|}\times\int_0^{\infty}db\,b\frac{\exp[-2\,\mathrm{Im}\phi(t_s)]}{|(1-b^2/R_s^2)|^{1/2}}\ . \tag{6}$$

The evaluation of the impact-parameter integral depends on whether or not the phase at the saddle point has an imaginary part. Saddle points with $\mathrm{Im}\phi(t_s) = 0$ correspond to stationary phase points and are responsible for the quasistatic wing. If a root R_s is real then the associated saddle points t_s are on the real t axis hence the phase is real provided $b\leq R_s$ [see Eq. (4)]. Setting $\mathrm{Im}\phi(t_s)=0$ in Eq. (6) and truncating the impact-parameter integral at $b=R_s$ obtain

$$\gamma_c(\Delta)=n_p\Delta^2\sum_{R_s}\frac{8\pi^2R_s^2\hbar}{|V_d'(R_s)|}\ , \tag{7}$$

where the sum is over real roots of $\hbar\Delta=V_d(R_s)$. Impact parameters $b>R_s$ and any complex roots R_s make exponentially small corrections to Eq. (7). If the collision-broadening rate $\gamma_c(\Delta)$ is large compared to the spontaneous decay rate γ_N then the absorption profile Eq. (1) becomes

$$I(\Delta)=n_p\sum_{R_s}\frac{4\pi R_s^2\hbar}{|V_d'(R_s)|} \tag{8}$$

in agreement with usual quasistatic theory[2,3] except for the absence of a Boltzmann factor. The neglect of the Boltzmann factor in our result is due to the use of straight-line trajectories.

When there are no real rooots to the saddle-point condition $\hbar\Delta=V_d(R_s)$, the far wing line shape is determined by the complex roots. In this case the phase has an imaginary part. The main contribution to the impact-parameter integral in Eq. (6) then comes from regions of b where $\mathrm{Im}\phi(t_s)$ takes its smallest positive values. This occurs for small impact parameters $b<<|R_s|$ hence it is appropriate to use a small impact-parameter expansion of $\mathrm{Im}\phi(t_s)$. That small impact parameters give the dominant contribution may be anticipated by the following argument. When $|\Delta|T_d>>1$ and there are no stationary phase points, the phase ϕ is rapidly varying throughout the collision. Then according to Eq. (2) collisions which produce comparably large Fourier components of the difference potential will contribute to the broadening. Collisions with small impact parameters produce large Fourier components. Note also that high-velocity collisions produce large Fourier components hence velocity averaging will be important.[9] Expanding $\mathrm{Im}\phi(t_s)$ for small impact parameters gives after a straightforward calculation

$$\mathrm{Im}\phi(t_s)=\Phi_0+\frac{b^2}{2|R_s|^2}\Phi_2+\cdots\ ,$$

where

$$\Phi_0=\Delta\frac{\mathrm{Im}R_s}{v}-\mathrm{Im}\int_{\mathrm{Re}R_s}^{R_s}\frac{dR}{v}\frac{V_d(R)}{\hbar}\ ,$$
$$\Phi_2=-\mathrm{Im}\int_{\mathrm{Re}R_s}^{R_s}\frac{dR}{v}\frac{|R_s|^2}{R}\frac{V_d'(R)}{\hbar}\ , \tag{9}$$

with $R_s=\mathrm{Re}R_s+i\,\mathrm{Im}R_s$ determined by $\hbar\Delta=V_d(R_s)$. Using these results the impact-parameter integral in Eq. (6) is evaluated by the method of Laplace[7] to yield

$$\gamma_c(\Delta)=n_p\Delta^2\sum_{R_s}\frac{4\pi^2|R_s|^2\hbar}{|V_d'(R_s)|}\frac{\exp(-2\Phi_0)}{2\Phi_2}\ , \tag{10}$$

where Φ_0 and Φ_2 are given above and only the complex roots R_s for which Φ_0, $\Phi_2 > 0$ are included in the sum. This is the leading order asymptotic approximation to the broadening rate for antistatic regions of the line shape.

For power-law difference potentials $[V_d(R) = \pm\hbar \mid C_n \mid R^{-n}]$ with even n the integrals for Φ_0 and Φ_2 are easy to evaluate:

$$\Phi_0 = \frac{n}{n-1}\sin\left[(2k+1)\frac{\pi}{n}\right] \mid C_n \mid^{1/n} \frac{\mid \Delta \mid^{1-1/n}}{v}, \quad k = 0,1,\ldots,\frac{(n-2)}{2}$$

$$\Phi_2 = \frac{n}{n+1}\sin\left[(2k+1)\frac{\pi}{n}\right] \mid C_n \mid^{1/n} \frac{\mid \Delta \mid^{1-1/n}}{v}, \quad k = 0,1,\ldots,\frac{(n-2)}{2} .$$

The main contribution comes from the smallest value of Φ_0, namely, $k=0$ and $k=(n-2)/2$ in the expressions above, hence

$$\gamma_c(\Delta) = n_p R_0^2 v \frac{a_n}{\mid \Delta T_0 \mid^{2/n}} \exp(-b_n \mid \Delta T_0 \mid^{1-1/n}) , \tag{11}$$

$$R_0 = \left[\frac{\mid C_n \mid}{v}\right]^{1/n-1}, \quad T_0 = \frac{R_0}{v}, \quad a_n = \frac{4\pi^2(n+1)}{n^2 \sin\frac{\pi}{n}},$$

$$b_n = \frac{2n}{n-1}\sin\frac{\pi}{n} .$$

R_0 is the characteristic interaction length and T_0 the corresponding collision duration. The main feature is the exponential decrease of the broadening rate as $\mid \Delta T_0 \mid$ increases. The exponential decrease of the antistatic wing for power-law difference potentials was predicted by Holstein in unpublished works.[10] Tvorogov and Fomin[11] have also obtained results for power-law potentials with $n=6$ and $n=8$. However, their work contains some numerical errors.[11] We emphasize that Eq. (11) is the *leading order* asymptotic approximation to the broadening rate for the antistatic wing—the error of this approximation is of order $\mid \Delta T_0 \mid^{-n/(n-1)}$.

We now discuss the principal effects of averaging over a thermal distribution of relative velocities. The thermally averaged rate is calculated by integrating the rate for a given velocity times the velocity distribution:

$$\langle \gamma_c(\Delta) \rangle = \int d^3v f(v) \gamma_c(\Delta) .$$

The antistatic wing broadening rate Eqs. (9) and (10) is strongly velocity dependent due to the 1/v factor in the exponent Φ_0. The velocity integral is evaluated by the method of Laplace[7] and yields

$$\langle \gamma_c(\Delta) \rangle = n_p \Delta^2 \sum_{R_s} \frac{8\pi^2 \mid R_s \mid^2 \hbar}{\mid V_d'(R_s) \mid} \frac{\Phi_0(v_{\text{th}})}{\sqrt{3}\Phi_2(v_{\text{th}})} \times \exp(-3[\Phi_0(v_{\text{th}})]^{2/3}) , \tag{12}$$

where $\Phi_0(v_{\text{th}})$ and $\Phi_2(v_{\text{th}})$ are given by Eq. (9) with v replaced by $v_{\text{th}} = \sqrt{2kT/\mu}$ and the sum over R_s includes only those values for which $\Phi_0(v_{\text{th}})$, $\Phi_2(v_{\text{th}}) > 0$. A certain range of velocities (depending on Δ) makes the dominant contribution to the broadening. This is due to the balance between the broadening rate which increases rapidly as v increases and the velocity distribution which decreases rapidly as v increases.

The result for $\langle \gamma_c(\Delta) \rangle$ is closely related to the thermally averaged antistatic profile given by Szudy and Baylis.[2] These authors use a quadratic expansion of the potential in the neighborhood of the saddle point. The motivation for this is that it enbles analytic results valid uniformly for the usual quasistatic case and also in the region near a satellite. We can recover the Szudy-Baylis antistatic profile (except for a Boltzmann factor and a multiplicative factor[12]) by using a quadratic expansion of the potential to approximately evaluate $\Phi_0(v_{\text{th}})$, $\Phi_2(v_{\text{th}})$ in Eq. (9). This type of approximation can lead to subtantial error because $\Phi_0(v_{\text{th}})$ appears in the exponent in Eq. (12). The use of a quadratic expansion can only be expected to yield good results if the complex roots R_s are close to the real axis.

For power-law potentials $[V_d(R) = \pm\hbar \mid C_n \mid R^{-n}]$ the thermally averaged broadening rate is

$$\langle \gamma_c(\Delta) \rangle = n_p R_{\text{th}}^2 v_{\text{th}} \alpha_n \mid \Delta T_{\text{th}} \mid^{1-3/n} \times \exp[-3(\beta_n \mid \Delta T_{\text{th}} \mid^{1-1/n})^{2/3}] , \tag{13}$$

$$R_{\text{th}} = \left[\frac{\mid C_n \mid}{v_{\text{th}}}\right]^{1/n-1}, \quad T_{\text{th}} = \frac{R_{\text{th}}}{v_{\text{th}}},$$

$$\alpha_n = \frac{16\pi^2(n+1)}{n(n-1)\sqrt{3}}, \quad \beta_n = \frac{n}{n-1}\sin\frac{\pi}{n} .$$

Formin and Tvorogov[13] have obtained similar results for $n=6$ and $n=8$ by averaging their previous results[11] over a Maxwell-Boltzmann velocity distribution. They report correct numerical factors in the exponent (β_n) but different multiplicative factors.[11] Comparing Eqs. (11) and (13) it is apparent that velocity averaging substantially affects the detuning dependence of the line shape.

CONCLUSION

We have applied the saddle-point technique to obtain asymptotic approximations to the collision-broadening rate $\gamma_c(\Delta)$. An exponentially decreasing broadening rate results when the phase at the saddle point has an imaginary part. Velocity averaging substantially affects these antistatic regions of the line shape due to the strong velocity dependence of the broadening rate. The results in this report expand the range of detunings covered by simple analytic approximations to the collision-broadening rate.

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[12]Instead of the factor $\cos^2\theta$ in the results of Szudy and Baylis we have a factor of $\frac{2}{3}$ when using expansion Eq. (7.9) of Ref. 2. For a purely quadratic potential our results agree exactly with Ref. 2 to within terms of order $(\mathrm{Im}R_s/\mathrm{Re}R_s)^2$, i.e., for R_s close to the real axis.

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