Collisional line broadening due to van der Waals potentials

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The thermally averaged collision-broadened line shape is written in terms of a detuning-dependent broadening rate \( \gamma_{\text{c}}(\Delta) \) which is evaluated numerically for van der Waals potentials using classical straight trajectories. The results are presented in terms of reduced variables that make it easy to calculate the line shape for any system with arbitrary van der Waals coefficient and temperature. The results show how the line shape makes a smooth transition from a Lorentzian profile in the impact region to the dramatically asymmetric far line wings. The transition zone is characterized by \(|\Delta|T_d \sim 1\), where \( \Delta \) is the frequency detuning from resonance and \( T_d \) is a characteristic collision duration. The lowest-order correction to the Lorentzian line shape due to finite collision duration describes the dominant behavior for \(|\Delta|T_d \sim 1\). The numerical results are compared with analytic approximations and recent experiments. Averaging over a thermal distribution of relative velocities is shown to alter the line-shape asymmetry substantially, improving agreement between theory and experiment. The temperature dependence of the overall line shape is presented and discussed.

INTRODUCTION

The absorption line shape for an isolated optical transition in a dilute gas can be written as a generalized Lorentzian profile with a detuning-dependent collision broadening rate \( \gamma_{\text{c}}(\Delta) \) (Refs. 1–4):

\[
A(\Delta) = \frac{1}{2\pi} \frac{\gamma_N + \gamma_{\text{c}}(\Delta)}{(\Delta - \delta_{\text{c}})^2 + [\gamma_N + \gamma_{\text{c}}(0)]^2/4},
\]

where \( \Delta = \omega - \omega_0 \) is the detuning from resonance. The natural width due to radiative decay is \( \gamma_N \), and \( \delta_{\text{c}} \) is the collision-induced line shift. The detuning dependence of \( \gamma_{\text{c}}(\Delta) \) accounts for deviation from a simple Lorentzian profile for frequencies beyond the impact region. The frequency scale for the variation of \( \gamma_{\text{c}}(\Delta) \) with detuning is \( T_d^{-1} \), where \( T_d \) is a characteristic collision duration \( (T_d \sim 10^{-12} \text{ sec}) \), so that \(|\Delta|T_d \sim 1\) for \( |\Delta| \sim 5.3 \text{ cm}^{-1} \).

Near resonance \(|\Delta|T_d \ll 1\), the broadening rate is approximately constant, and the generalized profile above reduces to the familiar Lorentzian line shape of the impact theory.\(^{5}\) In the far wings of the line \(|\Delta|T_d \gg 1\), the broadening rate varies with detuning in a complex fashion that depends critically on the difference between the upper and lower state interaction potentials, \( V_d(R) \).

The transition of the collision-broadened line shape from the Lorentzian profile in the impact region to the far-wing profiles has received rather little attention in the literature. One of the few theoretical studies to examine this transition region is that of Srivastava and Zaidi,\(^6\) which considered the resonance broadening of a transition between two excited states due to collisions with identical atoms in the ground state. In this case there is a pair of long-range interaction potentials \( V_d(R) = \pm C_3R^{-3} \), and the far wings are symmetric about line center, falling off as \(|\Delta|^{-2} \) but with an amplitude different from that predicted by the impact theory.

The situation is dramatically different in the case of foreign-gas broadening, for which there is a single long-range difference potential that varies as \( R^{-6} \) due to the van der Waals interaction. The excited state potential is typically more attractive than that for the ground state; this gives rise to asymmetric far line wings, neither of which falls off as \(|\Delta|^{-2} \). On the quasistatic side (the red side for an attractive difference potential), the analytic form for the line shape is \(|\Delta|^{-3/2} \) for van der Waals broadening, implying that \( \gamma_{\text{c}}(\Delta) \propto |\Delta|^{-1/2} \). On the antistatic side, the line falls off faster than exponentially in \(|\Delta| \), reflecting the rapid decrease of \( \gamma_{\text{c}}(\Delta) \).\(^8\)

In this work, we evaluate the line shape numerically for broadening by a van der Waals potential using straight classical trajectories for the atom perturber motion. These restrictions limit the applicability of the results to systems with strong van der Waals interactions and detunings not too far from resonance (\(|\Delta| \ll kT\)). We express the results in terms of a simple pair of reduced variables so that
they may be applied to a system with arbitrary $C_6$ and temperature and show that thermal averaging, which has been omitted from previous theories although it is an inherent feature of all experiments, improves the agreement between the calculated and observed values of the first-order asymmetry parameter $a_1$. Moreover, we show that this first-order term by itself gives an excellent approximation to the line shape in the region $|\Delta|T_d \sim 1$, thereby bridging the gap between the Lorentzian core and the analytic approximations valid in the far line wings.

**BACKGROUND**

The detuning-dependent broadening rate for straight classical trajectories is:

$$
\gamma_\epsilon(\Delta) = \left\{ n_p \int_0^\infty 2\pi b \, db \int_{-\infty}^\infty dt \, \omega_d[R(t)] \exp \left[ i \Delta t - \int_{-\infty}^t dt' \omega_d[R(t')] \right] \right\}^2,
$$

where the angle brackets denote an average over relative velocities $v$, $n_p$ is the perturber density, $b$ is the impact parameter, and $\omega_d[R(t)]$ is the difference between the excited- and ground-state potentials seen on the trajectory $R(t) = (b^2 + v^2 t^2)^{1/2}$. The broadening rate Eq. (2) can easily be derived using the ideas of the Anderson model of line broadening, and it corresponds to the classical limit of the unified Franck-Condon theory of Szudy and Baylis. There is also a very close relationship between Eq. (2) and the rate of collisional transfer between dressed-atom states.

Yeh and Berman have presented calculations of the cross section for collisional transfer between dressed-atom states due to a van der Waals interaction. Our treatment differs from theirs in several significant ways: We explicitly average over a thermal distribution of collision velocities and present results for $\gamma_\epsilon(\Delta)$ in terms of an appropriately scaled function valid for any $C_6$ and temperature. Peach has given numerical data from which complete line shapes for van der Waals broadening can be calculated.

$$
I(\Delta T_d) = \int_0^\infty \frac{4}{\pi} u \exp(-u^2) du \int_0^\infty dr \, r^{-9} \left| \int_0^{\pi/2} d\theta \cos^4(\theta) \cos[\psi(\theta)] \right|^2,
$$

where

$$
\psi(\theta) = \frac{\Delta T_d r \tan \theta}{u} + \frac{W_6(\theta)}{u^5}.
$$

The dimensionless variables are $u = v/v_{ih}$, $r = b/R_{ih}$, $\tan \theta = ut/b$. The function $W_6$ is

$$
W_6(\theta) = \int_0^\theta d\phi \cos^4 \phi = \frac{3\theta}{8} + \frac{\sin(2\theta)}{4} + \frac{\sin(4\theta)}{32}.
$$

In Eq. (4) the integral over $u$ is the Maxwell-Boltzmann velocity average, the integral over $r$ is the impact parameter integration, and the integral over $\theta$ is the time integration for a trajectory with given impact parameter and velocity. We have written $I(\Delta T_d)$ explicitly as a function of $\Delta T_d$, the product of the detuning and the collision duration, where $T_d$ is defined by $T_d = R_{ih}/v_{ih} = |C_6|^{1/6}v_{ih}^{-6/5}$. We concentrate on the intermediate detuning range $\Delta T_d \sim 1$ where the transition between the impact region ($|\Delta T_d| \ll 1$) and the far line wings ($|\Delta T_d| \gg 1$) occurs.

**COMPUTATIONAL METHOD**

The numerical problem is to calculate $I(\Delta T_d)$ in Eq. (4) as a function of the parameter $\Delta T_d$. Of the three integrations involved, only the impact parameter ($r$) integration is difficult, owing to the rapid oscillations of the integrand at small impact parameter. The integral over $\theta$ was done by Simpson's rule using 600 evenly spaced points, and the integral over $u$ (velocity average) was done by a six-point Gaussian method (Gauss-Laguerre). Fortunately, for $\Delta = 0$, each stage of the numerical evaluation could be tested against exact analytic expressions. This was very useful for determining appropriate step sizes and truncation techniques.

The impact parameter ($r$) integral was done by integrating towards $r = 0$ starting with a maximum value $r_{\max} = 2.2$ and using the trapezoidal rule with an initial interval $\Delta r = 0.005$. The interval was decreased each time the slope of the integrand changed sign until the sixth zero of the integrand was reached (see Fig. 1). For smaller impact parameters the oscillations were too rapid to follow, and a random-phase approximation was used. The
envelope of these rapid oscillations was approximated in two ways: (1) a quartic polynomial was constrained to go through the origin with the correct slope\textsuperscript{13} and through the last calculated maximum with a slope and curvature determined by the neighboring maxima; (2) a cubic spline (straight at the ends) was connected through all calculated maxima and through the origin. These two approximations are illustrated in Fig. 1. We believe that the quartic polynomial is somewhat more accurate because it has the correct slope at the origin, and therefore use the quartic approximation for the presentation of our results in the next section. A comparison of the results of the two approximations provides a rough estimate of the error in $I(\Delta T_d)$.

The error in our numerical calculations is known precisely only for $\Delta = 0$, where the net relative error in the calculated value of $I(0)$ is $\approx 3 \times 10^{-3}$. On the quasistatic side of the line ($\Delta < 0$), we expect the error to be comparably small (certainly $< 1\%$) because our two estimates of the small impact parameter contribution to $I(\Delta T_d)$ agree well and the other two integrations ($\theta, \mu$) present no difficulty. On the antistatic side of the line ($\Delta > 0$), the estimated error remains $< 1\%$ for $\Delta T_d < 1$, but rapidly increases for $\Delta T_d > 1$ due to the difficulty of determining the contribution from small impact parameters. For $\Delta T_d = 2.4$ we estimate $\leq 5\%$ error in the value of $I(\Delta T_d)$. Thus we could not push the calculations to large positive $\Delta T_d$ where the broadening rate decreases exponentially.\textsuperscript{6}

RESULTS AND DISCUSSION

The detuning dependence of the broadening rate $\gamma_e(\Delta)$ for attractive van der Waals difference potentials is illustrated in Fig. 2. The calculated points (+) are shown connected by a cubic spline (solid curve). There is a striking asymmetry between the red ($\Delta < 0$) and blue ($\Delta > 0$) sides of the line. The basic reason for this asymmetry is that during a collision the interatomic potentials shift the transition frequency monotonically towards the red; the frequency shift is $\omega_d = -|C_v| R^{-\delta}$ (note that the sign of the asymmetry would be reversed for a repulsive difference potential). The fact that the broadening rate exhibits a strong dependence on detuning implies that the absorption profile deviates substantially from a pure Lorentzian shape [for a pure Lorentzian $I(\Delta T_d) = I(0)$, a constant].

Near resonance (|$\Delta T_d | < 1$), the broadening rate varies linearly with detuning producing asymmetry in the near wings of the line.\textsuperscript{14–17} Our numerical calculations agree very well with the Taylor-series expansion of Eq. (4) up to the term linear in $\Delta T_d$ [$I(\Delta T_d) \approx 0.3380 - 0.2245 \Delta T_d$]. The linear approximation (dotted line in Fig. 2) corresponds to the impact limit (|$\Delta T_d | \to 0$) plus the lowest-order correction due to the finite collision duration.\textsuperscript{3} It is

\begin{figure}[h]
\centering
\includegraphics[width=\linewidth]{fig1.png}
\caption{Relative contributions to the broadening rate $\gamma_e(\Delta)$ from various impact parameters are shown for a fixed collision velocity ($v = 2.403 v_\text{th}$) and three detunings: $\Delta T_d = -2$ (upper curve), $\Delta T_d = 0$ (central curve), and $\Delta T_d = +2$ (lower curve). The left portions of these curves ($b/R_\text{th} < 0.42$) show two estimates of the envelope of the rapid oscillations which occur for small impact parameters; the solid curve is a quartic polynomial and the dashed curve is a cubic spline.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\linewidth]{fig2.png}
\caption{Dimensionless function $I(\Delta T_d)$ defined by Eqs. (4)–(6) is shown. The broadening rate $\gamma_e(\Delta)$ can be determined from this curve using Eq. (3). Numerically calculated points (+) are connected by a cubic spline (solid curve); the dotted line is a linear Taylor-series approximation for small $|\Delta T_d |$, and the dashed lines are asymptotic approximations for $|\Delta T_d | \gg 1$.}
\end{figure}
The broadening rate near resonance ($|\Delta T_d| < 1$) may be written in the intuitively appealing form 
\[ \gamma_c(\Delta) \approx \gamma_c(0)(1 + a_1|\Delta T_d|) \]
where $\gamma_c(0)$ is the Lorentzian width (full width at half maximum) of the impact theory, $T_d$ is a characteristic collision duration, and $a_1$ is a numerical coefficient. The value of the numerical coefficient depends on the definition of the collision duration $T_d$. For our definition $T_d = C_0 |1/\nu_{th}|^{1/2}$ with $\nu_{th} = (2kT/\mu)^{1/2}$, the calculation yields $a_1 = -0.664$. In the experiment of Walkup et al., the collision duration was defined in terms of the impact broadening rate and the rms relative velocity: $T_d = R_A/v_{rms}$ where $\gamma_c(0) = n_p \pi R_A^2 v_{rms}$ and $v_{rms} = (3kT/\mu)^{1/2}$. With these definitions, $\gamma_c(\Delta) = \gamma_c(0)(1 + a_1|\Delta T_d|)$, where $a_1 = -0.547$ for attractive van der Waals broadening. This compares favorably with the average value of $a_1$ reported experimentally: $a_1^{(exp)} = -0.53 \pm 0.08$ where the average is over the heavy perturbers Ar, Kr, and Xe and both of the Na D lines.

We emphasize that the asymmetry in the near wings is sensitive to velocity averaging since the lower velocity collisions have a longer effective collision duration. Predictions of near-wing asymmetry that do not use the proper velocity average generally underestimate the asymmetry; using a constant relative velocity, one would predict $a_1 = -0.420$, a value significantly different from the velocity-averaged result of $a_1 = -0.547$ for attractive van der Waals broadening.

CONCLUSIONS

Interaction by van der Waals potentials produces a strongly detuning-dependent collision broadening rate $\gamma_c(\Delta)$. Near resonance ($|\Delta T_d| < 1$), $\gamma_c(\Delta)$ is well approximated by the impact broadening rate plus a linear correction due to the finite collision duration: 
\[ \gamma_c(\Delta) \approx \gamma_c(0)(1 + a_1|\Delta T_d|) \]
The linear term accounts for the asymmetry in the near line wings, and it describes the

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**FIG. 3.** Temperature dependence of $\gamma_c(\Delta)$ is illustrated. The parameters have been chosen such that $T_d^{-1}$ corresponds to 5 cm$^{-1}$ at $T = 400$ K. The relative broadening rate shown is the ratio of $\gamma_c(\Delta; T)$ to $\gamma_c(\Delta = 0; T = 400$ K). The quasistatic approximation is temperature independent and is shown as a dashed line.
dominant behavior of $\gamma_e(\Delta)$ in the intermediate zone ($|\Delta T_d| \sim 1$) between the impact region and the far line wings. The goodness of the linear approximation is related to the presence of a smooth monotonic potential. For systems where both the long-range attractive and short-range repulsive parts of the potentials contribute, a more complex behavior is to be expected, even in the near line wings (see for example the Na-N$_2$ data of Jongerius et al.\textsuperscript{16}). The broadening rate for van der Waals potentials makes a smooth transition (with no undulations) from the linear behavior near resonance to the asymptotic behavior of the far line wings ($|\Delta T_d| \gg 1$). The quasi-static approximation is quite good even for moderate values of $|\Delta T_d|$; the error is $<3\%$ for $|\Delta T_d| > 2$. Averaging over a thermal distribution of relative velocities substantially affects the line shape near resonance and particularly on the antistatic far wing.

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\textsuperscript{7}The vast majority of experimental line broadening studies involve $S \rightarrow P$ transitions, for which there are generally two molecular potentials that correlate to the $P$ state (Σ and Π), although exceptions exist [e.g., Cs(6P$_{1/2}$)-Cs(6S$_{1/2}$), Ti(7S$_{1/2}$)-Ti(6P$_{1/2}$)]. However, nearly all theoretical treatments of line broadening assume that there is only a single potential in each state.


\textsuperscript{10}V. S. Lisitsa and S. I. Yakovlenko, Zh. Eksp. Teor. Fiz. 68, 479 (1975) [Sov. Phys.—JETP 41, 253 (1975)].


\textsuperscript{13}As $r \rightarrow 0$ the $r$ integrand $\rightarrow u'r \sin^2[W_0(\pi/2)/ur^2]$; hence the slope at the origin is $u^2$.


\textsuperscript{18}D. Perrin and J. C. Peannet, J. Phys. 42, 1607 (1981); also D. G. McCartan (private communication).