A Computational/Spectroscopic Study of a Newly Derived General Unified Theory of Spectral Line Shapes to Measure HWHM's for an Ar-perturber/K-radiator system, Using Two 7s ← 4p Transitions, as Applied to the Line Core

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Abstract: In a recent publication, a new unified theory of spectral line shapes was derived, which allowed for the variation of the electric dipole moment with perturber positions. The present author put the g(s) term derived from the theory into a computable form, and constructed spectral line shapes from which line-core HWHM's (w's) were measured. These w's were compared with experimental Fabry-Perot-interferometric results. Typically, for ΔV₂ and T=1000 K, the percent difference between w_expt. and w_compt. is ≈ 22%. log(w) − vs − log(P) and curve is computed and compared with those from non-impact-approximation-theory computations. Two temperatures were studied at T=400 and 1000 K in the Ar-perturber/K-radiator system; and two pseudo-potential differences were used: 1) V_Δ = 22 1/2 3/2,3/2,7 and 2) V_Δ = 3/2,1/2 2 1/2 2 47 PpSs. They were used to evaluate their comparative effects on w. E.g., ΔV_1 with a deep well exhibited a larger w than that of ΔV_2 with a shallow well.

Keywords: Quantum-mechanical, Semi-classical, Unified-theory, Spectral-line-shapes, Non-impact-approximation, K/Ar-system.

1. INTRODUCTION

In the continual development of spectral line-shape theory, one of the most important outputs of a theory is the derivation of the g(s) term, defined in the Discussions subsection 6.3, because from it the line shape can be computed and the HWHM(w) can be measured and tested experimentally with spectrophotometric or interferometric techniques. Typical derivations of the g(s) term are as follows: Baranger [1] derived two quantum-mechanical (QM) g(s) terms, one Eq.(31)[1] for the impact approximation and one Eq.(29)[1] for the non-impact approximation; Allard and Kielkopf [2] derived two semi-classical (SC) g(s) terms, two Eqs.(56,57)[2] for the impact approximation and one Eq.(55)[2] for the non-impact approximation; Szudy and Baylis [3] presented a g(s) term Eq.(2.15) [3] for their unified theory; very recently, Allard et al. [4] published a comprehensive derivation of the g(s) term Eq.(121) [4] for their unified theory of line shapes, in which the electric dipole moment varies with the position of the perturbers (see Theory Section for details of the theory). An example of the application of this unified theory is by Allard et al. [5] who studied the He(3S) − He(2P) line.

Kreye and Kreye/Kielkopf [6-9] have used the g(s) terms to compute spectral-line shapes for the line core; and from them have measured the w's and the shifts d's of the 5802 Å line for the Ar-perturber/K-radiator system at temperatures (T's) equal to 400, 800 and 1000 K. They computed and discussed log(w) − vs − log(P) and log(w) − vs − log(n) curves for two pseudo-potential differences, ΔV₀ = plane wave − 4p²P₁/2,1/2, and ΔV₁ = 7s²S₁/2 − 4p²P₁/2,1/2. P and n are the perturber pressure and density, respectively.

In the present paper, Kreye extends the previous studies [6-9] as follows:(1) the g(s) term from the newly derived unified theory of spectral line shapes Eq.(121)[4] is put into a computable form and the w's are measured from the computed line shapes for the line core;(2) a computed non-impact-approximation log(w) − vs − log(P) curve is compared...
with an earlier impact-approximation curve in [8]; (3) a third pseudo-potential difference is introduced, \( \Delta P_{2} = 7s^{2}S_{1/2} - 4p_{2}P_{3/2,1/2} \); (4) \( \log(w) - vs - \log(P) \) curves for the unified theory are studied at \( T = 400 \) and \( 1000 \) K and compared with those from non-impact-approximation theory; (5) a question had been brought up in the previous paper [9], which shows in Fig. (2) [9] a slope discontinuity in the \( \log(w) - vs - \log(P) \) curve between the impact-approximation and non-impact-approximation regions. The question was, is there any alternative method for plotting \( \log(w) - vs - \log(P) \) curves which avoids the slope discontinuity? This paper shows that there is an alternate method for plotting \( \log(w) - vs - \log(P) \) that avoids these slope discontinuities, as demonstrated in Fig. (3) and in Conclusions 5.1.

2. THEORY

2.1. Impact-approximation and Non-impact-approximation Theories

In the present paper, the SC impact-approximation Eqs.(56,57) [2] and the non-impact-approximation Eq.(55) [2] are used in computing \( \log(w) - vs - \log(P) \) curve.

2.2. Unified Theory

Theoretical calculations and experimental evidence show that the electric dipole transition moment is not constant [10]. Allard et al. [4] derived a unified theory of spectral line shapes to take into account the dependence of the electric dipole moment upon the position of the perturbers. The details of the complete derivation are given in [4].

The important \( g(s) \) term in the unified theory is given in Eq.(121)[4]. It is renumbered here as Eq.(1) and includes several minor changes: only one transition is considered and the first factor on the right of Eq.(121)[4] is taken as unity.

\[
\begin{align*}
\Re \sqrt{2} & = \int_{0}^{\infty} 2\pi d\rho \int_{0}^{\infty} d\rho \cdot \tilde{d}_{e,s}[r(0)] \cos(h\int_{0}^{\infty} dV_{p,s}[r(t)]) \\
\tilde{d}_{e,s}[r(s)] & - \tilde{d}_{e,s}[r(0)],
\end{align*}
\]

where \( \Re \sqrt{2} \) has been formed from Eq.(121)[4] by using the real part of \( \exp(ih^{1}...) \), namely, \( \cos(h^{1}...) \). In order to put \( \Re \sqrt{2} \) Eq.(1) into a computable form, we must first put \( \Re \sqrt{2} \) into a computable form. We substitute the electronic basis function \( \psi_{f,s}(r) \) Eq.(14)[8] for the \( \chi_{e^*}(\vec{r}) \) term in Eq.(93)[4] and \( \psi_{f,s}(r) \) for the \( \chi_{e^*}(\vec{r}) \) term in Eq.(93)[4]. \( \Re \sqrt{2} \) then becomes

\[
d_{e,s}(r) = \langle \psi_{f,s}(r) | d | \psi_{f,s}(r) \rangle,
\]

where \( d \) is generally approximated as unity. \( \psi_{f,s}(r) \) was introduced in [8] as Eq.(14). Renumbered, it becomes

\[
\psi_{f,s}(r) = \sum_{i=0}^{\infty} \frac{(2l+1)i^{i}}{i!} \exp(i\delta_{i,s})R_{l,i}(kr)P_{l}(\cos\theta),
\]

where \( \psi_{f,s}(r) \) has been expanded as a sum of partial waves. \( l \) is the angular momentum quantum number, \( \delta_{i,s} \) is the phase shift, \( P_{l}(\cos\theta) \) is the Legendre polynomial and \( R_{l,i}(kr) \) is the solution to the Schroedinger equation Eq.(6)[9], renumbered below as Eq.(4), and expressed in \( R_{l,i}(kr) \) terms:

\[
d^{2}R_{l,i}/d\rho^{2} + 2dR_{l,i}/\rho d\rho + [1 - 4\mu\nu V_{1}(\rho)/\hbar^{2} - l(l+1)/\rho^{2}]R_{l,i} = 0,
\]

where \( k = \sqrt{2\mu k_{B}T}/\hbar^{2} \), \( \mu \) is the reduced mass and only in Eq.(4), \( \rho = kr \). Note that in Eq.(1) and in the following equations, \( \rho \) is the impact parameter.

Of the two forms, \( d_{e,s}[r(0)] \) and \( d_{e,s}[r(s)] \), we choose \( d_{e,s}[r(0)] \) to derive, where \( r(0) = \sqrt{\rho^{2} + x^{2}} \) and \( x \) is the position of the perturber along its straight-line trajectory. For a given \( \rho \), \( x \) and the corresponding \( kr(0) \), the Schroedinger Eq.(4) is scanned through 2750 solutions until the value of the independent variable \( \rho \) matches the above value of \( kr(0) \). The corresponding value of the dependent variable, \( R_{l,i}[kr(0)] \), is the desired term for Eq.(5) below. Similarly, we use \( V_{1}(\rho) \) in Eq.(4) to get \( R_{l,i}[kr(0)] \) for Eq.(5).

The dipole matrix \( d_{e,s}[kr(0)] \) in Eq.(2) involves an integration over \( \theta \) of the product \( \psi_{f,s}[kr(0)] \cdot \psi_{f,s}[kr(0)] \) (the integration over \( \varphi \) equals \( 2 \pi \)). Now from Eq.(3), this product involves a double sum, \( \sum_{l=0}^{l_{\text{max}}} \sum_{s=0}^{s_{\text{max}}} \tilde{d}_{e,s}(r) \tilde{d}_{e,s}(r) \). The \( \theta \) integration of Eq.(2), after \( \psi_{f,s}(r) \) and \( \psi_{f,s}(r) \) from Eq.(3) have been entered, the orthogonality of \( P_{l}(\cos\theta) \cdot P_{l}(\cos\theta) \) eliminates one sum. The resulting integration over \( \theta \) of the remaining sum yields

\[
d_{e,s}[kr(0)] = \sum_{l=0}^{l_{\text{max}}} \sum_{s=0}^{s_{\text{max}}} (2l+1)^{2} \bar{d}_{e,s}(r) R_{l,s}[kr(0)] R_{l,s}[kr(0)].
\]

Similarly, one obtains an expression for \( d_{e,s}[r(s)] \) for a given value of \( s \), where \( r(s) = \sqrt{\rho^{2} + (x + vs^{2})^{2}} \) and where the velocity \( v = \sqrt{3k_{B}T/\mu} \). The integration over \( dt \) can be achieved in Eq.(1) if we set the expression for \( r(t) \) equal to \( \sqrt{\rho^{2} + (x + vt)^{2}} \). From Eq.(117)[4],

\[
\tilde{d}_{e,s}(r) = d_{e,s}(r) \cdot \exp[b/2k_{B}T \cdot V_{1}(r)].
\]

Thus, we have all the necessary terms for the three integrations in Eq.(1) to form \( \Re \sqrt{2} \) for a given \( s \). Note, \( R_{l,i}[kr(0)] \) and \( R_{l,i}[kr(0)] \) are implicit functions of \( \rho \) and \( x \), and \( R_{l,i}[kr(s)] \) and \( R_{l,i}[kr(s)] \) are implicit functions of \( \rho \), \( x \) and \( s \). Similarly, we obtain \( \Im \sqrt{2} \) by substituting \( \sin(h^{1}...) \) for \( \cos(h^{1}...) \) in Eq.(1). Finally, the line shapes
for different P’s, can be computed from the following line-shape equation \( F(\omega) \):
\[
F(\omega) = \frac{2}{2\pi} \int_{0}^{\pi} \exp\{-n \cdot \Re [g(s)]\} \cos\{-n \cdot \Im [g(s)] + \omega s\}. 
\]

(6)

Thus, the desired computed \( w \)’s can now be obtained from measurements made on these line shapes, and these computed values of \( w \) can be put into the curves as shown in the Results Section.

3. COMPUTATIONAL DETAILS

3.1. Integration of Eq.(4)

The integration of the Schroedinger Eq.(4) to obtain \( R_{ij}([kr(0)], R_{ij}[kr(0)], R_{ij}[kr(s)] \) and \( R_{ij}[kr(s)] \) used a second-degree Runge-Kutta method;

3.2. Expansion of Pseudo-potentials

The pseudo-potentials were expanded into 2750 elements employing a standard Spline technique;

3.3. Plotting of \( \log(w) - \log(P) \) curves

For a given value of \( P \) and of \( T \), the value of \( w \) was measured from the computed line shape, \( F(\omega) \) Eq.(6). The resulting \( w \)’s for different \( P \)’s were plotted as \( \log(w) - \log(P) \) curves. This type of a plot was used because it is linear in the case of the impact-approximation Eqs.(56,57)[2], thus allowing the slope to be easily measured and characterized;

3.4. Choice of \( l_{\text{max}} \)

The choices of \( l_{\text{max}} = 160 \) and 105 are for \( T=1000 \) and 400 K, respectively;

3.5. Choice of \( s_{\text{max}} \) at \( T=400 \) K

For the computations of \( \log(w) \) at \( T=400 \) K, we used the following procedure: the value of \( s_{\text{max}} \) at \( T=400 \) K is such that \( w \) at \( T=400 \) K equals \( w \) at \( T=1000 \) K=0.25 cm\(^{-1}\). This procedure is based on the results in [8], where Fig. (2) [8] established that the difference between \( w \) at \( T=400 \) K and \( w \) at \( T=1000 \) K was \( \approx 0.25 \) cm\(^{-1}\);

3.6. Integration of Eq.(6) over \( ds \)

For the integration over \( ds \) of Eq.(6) to obtain the line shape \( F(\omega) \), a value of \( s_{\text{max}} \) was used instead of the \( \infty \). Because of the close resemblance of the \( \int dt \) factor in Eq.(121)[4] to the \( \int dt' \) factor in the non-impact-approximation Eq.(55)[2], the following procedure was used: for a given \( P \), the value of \( s_{\text{max}} \) in the unified treatment was set equal to the corresponding value of \( s_{\text{max}} \) in the non-impact-approximation treatment. The calculation of \( s_{\text{max}} \) in the non-impact-approximation treatment is described below in subsection 3.7. A grid of 100 elements was adequate to ensure convergence of the integration.

3.7. Calculation of \( s_{\text{max}} \) in the Non-impact-approximation Treatment

We summarize here the method for calculating the \( s_{\text{max}} \) values in the non-impact-approximation treatment: first, for \( \log(P)=6 \) \( n \cdot \Re [g(s)] \) in Eq.(6) \( \approx 5 \cdot r^{-1} \). For simplicity, let \( s_{\text{max}}[\log(P) = 6] \) be represented by \( s_{\text{max}}(6) \). Then, \( s_{\text{max}}(5) = s_{\text{max}}(6) \cdot \sqrt(10) \), \( s_{\text{max}}(4) = s_{\text{max}}(5) \cdot \sqrt(10) \), \( s_{\text{max}}(3) = s_{\text{max}}(4) \cdot \sqrt(10) \), \( s_{\text{max}}(2) = s_{\text{max}}(3) \cdot 10 \), \( s_{\text{max}}(1) = s_{\text{max}}(2) \cdot 10 \).

This procedure is based on the results of [9], where the slope of the non-impact-approximation curve is \( d\log(w)/d\log(P) \approx 0.5 \) and the slope of the impact-approximation curve is \( d\log(w)/d\log(P) \approx 1.0 \).

4. RESULTS

4.1. Pseudo-potential Descriptions

Figs (1 and 2) show the pseudo-potentials, \( \Delta V_{1} = 7s^{2}S_{1/2} - 4P^{2}P_{3/2,1/2} \), \( X^{2}\sum_{i=2}^{1} - A^2\Pi_{3/2} \) and \( \Delta V_{2} = 7s^{2}S_{1/2} - 4P^{2}P_{3/2,1/2} \), \( X^{2}\sum_{i=2}^{1} - B^2\sum_{i=2}^{1} \), where \( \Delta V = V_{1} - V_{1} \). (See [11] for a discussion of the electronic states, such as \( X^{2}\Sigma_{1/2} - A^2\Pi_{3/2} \)). In the region \( R \approx 12.5 \) Å, the pseudo-potentials are about equal, \( \approx -9.0, -8.3 \) cm\(^{-1}\); but at \( R \approx 6.3 \) Å, \( \Delta V_{1} \) has a much deeper well of \(-39.3 \) cm\(^{-1}\) as compared with the well, \(-8.8 \) cm\(^{-1}\), in \( \Delta V_{2} \). The similarity in the shapes of the two pseudo-potential-differences at \( R \approx 12.5 \) Å is attributed to the fact that both pseudo-potentials have the same final state, \( 7s^{2}S_{1/2} \); and the difference in well depths at \( R \approx 6.3 \) Å is attributed to the difference between \( 4P^{2}P_{3/2,1/2} \) and \( 4P^{2}P_{3/2,1/2} \). The development of the pseudo-potential is best described in [2], lines 1127-1129.

4.2. Figures, Showing Pseudo-potentials, \( \log(w) - \log(P) \), \( \log(w) - \log(n) \) and \( \vec{d}_{e,e'}[r(0)] - r(0) \) Curves

4.3. \( w_{\text{expt.}} \) vs \( w_{\text{comp.}} \) Relations

(a) \( w_{\text{expt.}} \) values

The experimental results were reported in [6] in which measurements were made by the author on a pressure-scanned Fabry-Perot interferometer described by Kreye and
Fig. (1). This figure shows $\Delta V_1 = 7 s^2 S_{1/2} - 4 p^2 P_{3/2,3/2}$ as a function of R. Both Figs. 1 and 2 are scaled to the same vertical axis, from -100 to 12.

Roesler [12]. Fig. (4) [6] shows experimental values of width/n in the square-symbol line as a function of T.  
(a1) T=400 K

>From Fig. (4) [6], the value of width/n=8.9x10^{-20} cm^2 at T=400 K.  
At P=10 torr,
**Fig. (3).** This figure shows two $\log(w) - \log(P)$ curves for the line core at $T=1000$ K. The solid line corresponds to the non-impact-approximation Eq.(55)[2] and the dashed line corresponds to the impact-approximation Eqs.(56,57)[2]. As expected, the impact-approximation line is linear, whereas the non-impact-approximation line approaches a constant slope at $P=10^6$ torr. Both curves are for $\Delta V'$. The smooth solid line, with no slope discontinuities, answers the question at the end of the Introduction Section, namely, can the non-impact-approximation $\log(w) - \log(P)$ curve be plotted with no slope discontinuities?

**Fig. (4).** This figure shows two $\log(w) - \log(P)$ curves. The dotted line corresponds to the important unified Eq.(121)[4]. It steadily increases at $P=10^6$ torr. The solid line corresponds to the non-impact-approximation Eq.(55)[2], and it begins to approach a constant slope. At $P=10^6$ torr, the ratio of the unified-theory value of $w$ to the non-impact-approximation-theory value is 1.12. Both lines correspond to $\Delta V'_2$ at $T=1000$ K.

$w_{equil} = 0.021 \text{ cm}^{-1}$.

>From Fig. (4) [6], the extrapolated value of width/n$=13.4 \cdot 10^{-20} \text{ cm}^2$ at $T=1000$ K. At $P=10$ torr,
Fig. (5). This figure shows two \( \log(w) - \log(P) \) curves. The dotted line corresponds to the unified Eq.(121)[4]. The solid line corresponds to the non-impact-approximation Eq.(55)[4]. At \( P=10^9 \) torr, the ratio of the unified value of \( w \) to the non-impact-approximation value of \( w \) is 1.66. Both lines correspond to \( \Delta V_1 \) at \( T=1000 \) K.

Fig. (6). This figure shows the \( \log(w) - \log(P) \) curve which is computed at \( T=400 \) K and for \( \Delta V_2 \). The solid line corresponds to the non-impact-approximation Eq.(55)[2].

\[ w_{\text{expt.}} = 0.013 \text{ \ cm}^{-1}. \]

(b) \( w_{\text{compt.}} \) values

The computed results for \( T=1000 \) K are based on analyses of spectral-line shapes for the unified theory and for the non-impact-approximation theory.

(b1) \( T=400 \) K
>From Fig. (6), with $\Delta V_2$ and $T=400$ K, the intersection of the solid non-impact-approximation line with the horizontal axis at $P=10$ torr yields $w_{\text{compt.}}=0.0281$ cm$^{-1}$.

(b2) $T=1000$ K

>From Fig. (4), with $\Delta V_2$ and $T=1000$ K, the intersection of the dotted unified line with the horizontal axis at $P=10$ torr yields $w_{\text{compt.}}=0.0159$ cm$^{-1}$.

(b3) $T=1000$ K

>From Fig. (5), with $\Delta V_1$ and $T=1000$ K, the intersection of the dotted unified line with the horizontal axis at $P=10$ torr yields $w_{\text{compt.}}=0.0229$ cm$^{-1}$.

(c) Percent difference = ($w_{\text{compt.}} - w_{\text{expt.}}$) / $w_{\text{expt.}}$.

>From the above data at $T=400$ K, we compare $w_{\text{expt.}}=0.021$ cm$^{-1}$ with $w_{\text{compt.}}=0.0281$ cm$^{-1}$. The percent difference is +33%, and the average value is 0.024 cm$^{-1}$. At $T=1000$ K, we compare $w_{\text{expt.}}=0.013$ cm$^{-1}$ with $w_{\text{compt.}}=0.0159$ cm$^{-1}$. The percent difference is +22%, and the average value is 0.014 cm$^{-1}$.

4.4. Ratios of $w_{\text{unif.}}$ / $w_{\text{non-impact-approximation}}$, Compared for $\Delta V_1$ and $\Delta V_2$

The ratio of $w_{\text{unif.}}$ / $w_{\text{non-impact-approximation}}$ at $T=1000$ K, $P=10^6$ torr and for $\Delta V_1$ is calculated from Fig. (5) in the present paper to be 1.66. The corresponding ratio for $\Delta V_2$ is calculated from Fig. (4) to be 1.12. The larger ratio for $\Delta V_1$ is attributed to its deeper well of -39.3 cm$^{-1}$ at $R \approx 6.3$ Å as compared to the corresponding well of -8.8 cm$^{-1}$ for $\Delta V_2$. $w_{\text{unif.}}$ is the value of $w$ for the unified theory.

4.5. Dependence of $w_{\text{unif.}}$ upon the Depth of the Well

For this result, $P=10$ torr, $T=1000$ K. We show in the following that the $w_{\text{unif.}}$ is an increasing function of the depth of the well: for a well depth of -8.8 cm$^{-1}$ in $\Delta V_1$, $w_{\text{unif.}}=135$ cm$^{-1}$; and for a well depth of -39.3 cm$^{-1}$ in $\Delta V_2$, $w_{\text{unif.}}=239$ cm$^{-1}$.

5. CONCLUSIONS

5.1. Objective one: to Eliminate the Slope Discontinuities in the Curves in Fig. (2) [9]

The slope discontinuities in the $\log(w) - vs - \log(P)$ curves in Fig. (2) [9] are a result of using two theories: the impact-approximation theory for small log(P) and the non-impact-approximation theory for large log(P). For each theory, there is a unique linear $\log(w) - vs - \log(P)$ line, as demonstrated in the two intersecting straight lines for each of the three temperature-plots in Fig. (2) [9]. In Fig. (3) in the present paper, there is only one plot for $T=1000$ K. However, the solid-line curve exhibits no slope discontinuity; this is a result of using the non-impact-approximation theory for the whole log(P) range.

5.2. Objective Two: to Show that a Deeper Well Will Yield a Larger Value of $w$

In subsection 4.5, $P=10$ torr and $T=1000$ K. For $\Delta V_2$ with a well depth of -8.8 cm$^{-1}$, $w_{\text{unif.}}=135$ cm$^{-1}$. For $\Delta V_1$ with a well depth of -39.3 cm$^{-1}$, $w_{\text{unif.}}=239$ cm$^{-1}$. Thus, the objective is fulfilled.

5.3. Objective Three: to Compare $w_{\text{expt.}}$ with $w_{\text{compt.}}$ and to Calculate the Percent Difference

From subsection 4.3(b2) with $P=10$ torr, $T=1000$ K and for $\Delta V_2$, $w_{\text{compt.}}=0.0159$ cm$^{-1}$. From subsection 4.3(a2) with $P=10$ torr and $T=1000$ K, $w_{\text{expt.}}=0.013$ cm$^{-1}$. >From subsection 4.3(c), the percent difference is $\approx 22\%$, thus fulfilling the objective.

5.4. Objective Four: to Show that the Value of $w$ for the Unified Theory is Larger than the Value of $w$ for the Non-impact-approximation Theory at $P=10^6$ Torr

From Fig. (5) at $P=10^6$ torr, $T=1000$ K and for $\Delta V_1$, $w_{\text{unif.}}=239$ cm$^{-1}$ and $w_{\text{non-impact-approximation}}=144$, cm$^{-1}$. Thus, the objective is fulfilled.

5.5. Objective Five: to Show that the Value of $w$ at $T=400$ K is Greater then the Value of $w$ at $T=1000$ K

From Fig. (6) at $T=400$ K, $P=10^7$ torr and for $\Delta V_2$, $\log(w_{\text{compt.}})=0.380 \log(cm^{-1})$. From Fig. (4) at $T=1000$ K, $P=10^7$ torr and for $\Delta V_1$, $\log(w_{\text{compt.}})=0.199 \log(cm^{-1})$, thus fulfilling the objective.

6. DISCUSSIONS

6.1. QM, SC contributions to Eq.(1)

Equation (1) essentially contains an SC part and a QM part. The SC part is given by the $\int_0^\infty dt V_{\text{sc}}(r(t))$ term in Eq. (1), since it is identical, in content, with the $\int_0^\infty dt V[(b^2 + x^2)^{1/2}]$ term in the SC Eq.(55)[2], renumbered as Eq.(7) below (if the $h^{-1}$ term is removed):

$$g(s) = 2\pi \int_0^\infty db \int_x^\infty dx_0 [1 - \exp(-t [h^{-1} V[(b^2 + x^2)^{1/2}]] dt')] ,$$

(7)

where $x = x_0 + vt$. The QM terms of Eq.(1) are $\tilde{a}_{\text{compt.}}[r(0)]$ and $\tilde{a}_{\text{expt.}}[r(s)]$. 
6.2. Comparison of $w_{\text{expt.}}$ with $w_{\text{compt.}}$

From Section 4.3, the percent differences between $w_{\text{expt.}}$ and $w_{\text{compt.}}$, 33% and 22%, are admittedly large; however, the corresponding average values, 0.024 and 0.014 cm$^{-1}$, are measures of the absolute values of $w$, since the computed values of $w$ are compared with experimental values.

In most studies, an average value is only a relative value, since it is a result of a comparison between a computed/theoretical value and a computed/theoretical value.

6.3. Definition of $g(s)$

Broadly speaking, the $g(s)$ term contains the intricate details of the basic theory in a form which is usable in the actual spectral-line-shape expression, $F(\omega)$, which has a general Gaussian/Lorentzian form.

The $g(s)$ term is included in the $F(\omega)$ line-shape Eq.(6). One of the simplest definitions is from the impact-approximation Eq.(31) [1], $g(s) = i\langle \tilde{k} | V | \psi^+ \rangle$, where the expression $\langle \rangle$ represents an integration over $\theta$, $\varphi$ and $r$. $\tilde{k}$ and $\psi^+$ are defined in Eqs.(9,14) [8]. $\Re[g(s)]$ is the real part of the complex $g(s)$.

CONFLICTS OF INTERESTS

The authors confirm that this article content has no conflicts of interest.

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