Statistical models of scalar collisional interference incorporating phase shifting

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Abstract. In this paper we include phase shifting in the simple statistical models of collision sequence interference developed earlier by the authors. The Lindholm model of shifting and broadening is used.

1. Scalar collisional interference
Scalar collisional interference is a phenomenon known principally in HD and its mixtures with hydrogen and rare gases, though it should also be found in HT and DT.

HD has a small permanent dipole moment and small transition moments. These are due to small breakdowns in the Born–Oppenheimer separation.

Perhaps the clearest of the HD spectra are shown in ref. [1]. Fig. 1 of [1] shows the overall spectrum around the fundamental band with the $P$, $Q$, and $R(0)$ and $R(1)$ branches clearly shown, and Fig. 2 of [1] shows the pressure dependence of the shape of the $R(0)$ band with a constant HD density of 14.5 amagat and He density varying from 29.4 amagat to 205 amagat. The inversion of the line shape with increasing He density can clearly be seen.

The “scalar interference” contribution to the $R$ and $P$ transitions is actually a combination, based upon two effects: an interference between the scalar-modulated internal dipole induced in collisions and the small permanent dipole allowed through a breakdown of the Born-Oppenheimer approximation in the mass-asymmetric HD molecule; and an interference between successive scalar–modulated collisionally induced internal dipole transition moments. The designation “scalar collisional interference” refers to the scalar nature of functions of intermolecular separation (which resemble the intermolecular energy function) that modulate the internal dipole. The collision dynamics of importance are those that influence these functions as the HD molecule experiences them throughout collision sequences. The internal dipole then contributes to $J = \pm 1$ transitions, and can interfere with any other scalarly modulated internal transition operator having dipole symmetry, including the permanent dipole itself.
2. Theoretical and computational studies
The observed line shapes are well fit by a dispersion function \([2, 3]\):

\[
A(\nu) = D_0 \frac{(1 + 2\Delta \nu/(q\Gamma))^2}{(1 + (2\Delta \nu/\Gamma)^2)}.
\]

Herman and coworkers \([2, 3]\) argued that

\[
q^{-1} = \rho_{FG} \Delta'' I / (1 + \rho_{FG} \Delta' I)
\]

with total intensity going as

\[
\tilde{\alpha}_1(\rho_{FG}) = \tilde{\alpha}_1(0) \left(1 + 2\rho_{FG} \Delta' I + \rho_{FG}^2 (\Delta'^2 - \Delta''^2) I^2 \right)
\]

and this fits the observational data of ref. \([1]\) and other studies within observational error, over the range of densities used.

Herman and coworkers provided little insight into the various parameters used in the above expressions. Extensive theoretical studies were carried out by J. Cooper and George Tabisz and co–workers (references can be found in the bibliography of \([4]\)) and a thorough computational study was performed by Magnus Gustafsson and Lothar Frommhold \([5]\). These have provided considerable understanding of the phenomenon at the level of few–body interactions.

3. On the usefulness of simple models
Simple soluble models have proved of inestimable value in the development of statistical mechanics. The first of these was the two–dimensional Ising model with zero field, which was solved by Lars Onsager in 1944 \([6]\).

The study of exactly soluble models, and models which were numerically tractable, was an essential component of the development of the study of critical phenomena in the 1960s and 1970s.

The study of line shapes, in contrast, has moved from simple (simplistic) models to more detailed and realistic ones, to good effect.

The reason is no mystery: correlated collective effects are not very important in typical spectra. Modelling atomic and molecular interactions in pairs and other small groups in great detail is, on the other hand, very important.

Collision–sequence interference offers one partial exception, because in collision–sequence interference the collision–induced spectra show (usually) sharp features which reflect correlations extending over several and in some instances many collisions.

4. “Simple stochastic models”
“Simple stochastic models” of collision–sequence interference are time series in which the actual molecular interactions are replaced with point pulses of integrated intermolecular force (i.e. impulses) and dipole moments.

Typically only one particle is followed. After each “interaction” its velocity is changed at random. The induced dipole moments or induced changes are represented as powers of the impulse.

The first and simplest of these stochastic models for collision–sequence interference was described in ref. \([7]\). That model was two–dimensional, with isotropic scattering, constant speed, and with fixed time steps between successive collisions, and looked only at vector collision–sequence interference.

Scalar interference was treated in the stochastic models in 2008 \([8]\).
It proved relatively easy to generalize to Gaussian velocity distributions, but always with zero persistence of velocity: the distributions of velocity before and after the collision are uncorrelated Gaussians, with the same temperature parameter. It also was straightforward to introduce simple Poisson distributions of intervals between collisions [9]. Collision time distributions do not confirm perfectly to simple Poisson distributions but are close to Poissonian [10, 11].

These models allowed estimation of the infilling of the vector interference dip by differences between the induced dipole moment and the intermolecular force, which is otherwise very difficult to obtain.

They also are useful for developing the numerical methods used to analyse molecular dynamics simulations which involve collision–sequence interference [12].

In these conference proceedings two enhancements of the models are described. The first is the extension from zero persistence of velocity to arbitrary persistence of velocity ($0 \leq \Delta < 1$). This is largely the work of H.T. Wheeler, and is reported elsewhere in these conference proceedings. The results are interesting but not unexpected – primarily a narrowing of the vector interference dip, predicted a long time ago [13].

The second enhancement is the incorporation of a line shifting mechanism into the model. In essence Lindholm broadening is used [14]. H$_2$ and HD are small nearly spherical molecules and a more elaborate mechanism is not justified in a first step.

5. Assumptions of the present model

It is assumed that $N$ collisions lie in the finite large time interval $(0, T)$,

$$0 \leq t_1 \leq \cdots \leq t_{N-1} \leq t_N \leq T.$$

These times are assumed to form a simple Poisson process: The intervals between collisions are assumed independent of velocity.

The velocity after collision $k$ is $v_{k+1}$. The impulse on collision $k$ (mass is unity) is

$$f_k = v_{k+1} - v_k.$$

6. Scalar modulation

The scalar modulation of the dipole moment absent shifting is given by

$$\mu(t) = \left[ A + \sum_k \mu_k \delta(t - t_k) \right] e^{-i\omega_0 t}$$

In these models, $\mu_k$ is expressed in terms of the impulse $f_k$. In full generality,

$$\mu_k = \mu_k[f_k]$$

but so far we have usually taken proportionality constant equal to unity:

$$\mu_k = f_k.$$

7. Phase shifting

During a collision the frequency of oscillation of the molecule shifts.

In more vigorous collisions, a nonradiative transition may take place, a possibility which can be ignored for simple models of the hydrogens.

We assume that during a collision $k$ the phase of the oscillation changes from $-i\omega_0 t$ to $-i\omega_0 t - \eta_k$. 

3
In the spirit of the simple stochastic models it is assumed that the shift in phase induced in a collision \(k\) is given by \(\eta_f = \eta [f_k]\). Usually we take

\[ \eta_f = \eta f_k. \]

where \(\eta\) is a real number.

Then the time dependence of the allowed part of the induced dipole moment modulation is given by

\[ \mu_A(t) = A e^{-i\omega_0 t - i\eta \varphi(t)} \]

\[ \varphi(t) = \sum_{k=1}^{N} f_k h(t - t_k) \]

where \(h\) is a Heaviside step function.

The induced part of the scalar modulation with phase shifting is

\[ \mu_i(t) = \sum_{k=1}^{N} f_k \delta(t - t_k) e^{-i\omega_0 t - i\eta \varphi(t)} \]

The total scalar modulation of the dipole moment becomes

\[ \mu(t) = \left[ A + \sum_{k=1}^{N} f_k \delta(t - t_k) \right] e^{-i\omega_0 t - i\eta \varphi(t)}. \]

The Fourier transform of \(\mu(t)\) is \(a_T(\omega)\).

We define

\[ \tilde{\alpha}(\bar{\omega}) = \left( e^{i\bar{\omega}t_1} - 1 \right) + e^{-i\eta f_1} \left( e^{i\bar{\omega}t_2} - e^{i\bar{\omega}t_1} \right) + e^{-i\eta(f_1 + f_2)} \left( e^{i\bar{\omega}t_3} - e^{i\bar{\omega}t_2} \right) + \ldots + e^{-i\eta(f_1 + \ldots + f_{N-1})} \left( e^{i\bar{\omega}t_N} - e^{i\bar{\omega}t_{N-1}} \right) + e^{-i\eta f_N} e^{i\bar{\omega}T} - e^{i\bar{\omega}t_N} \]

and the closely related function

\[ \hat{\alpha}(\bar{\omega}) = e^{i\bar{\omega}t_1} \left( 1 - e^{-i\eta f_1} \right) + e^{-i\eta f_1} e^{i\bar{\omega}t_2} \left( 1 - e^{-i\eta f_2} \right) + e^{-i\eta(f_1 + f_2)} e^{i\bar{\omega}t_3} \left( 1 - e^{-i\eta f_3} \right) + \ldots + e^{-i\eta(f_1 + \ldots + f_{N-1})} e^{i\bar{\omega}t_N} \left( 1 - e^{-i\eta f_N} \right) \]

The unaveraged periodogram can be written in terms of \(\tilde{\alpha}\) and \(\hat{\alpha}\):

\[ S_T(\omega) \equiv \frac{1}{T} |a_T(\omega)|^2 \]

\[ = \frac{1}{T} |A|^2 \left| \frac{\tilde{\alpha}(\bar{\omega})}{\bar{\omega}} \right|^2 + \frac{2}{T\eta} \Re A \frac{\hat{\alpha}(\bar{\omega}) \hat{\alpha}(\bar{\omega})^*}{\bar{\omega}} + \frac{1}{T\eta^2} |\hat{\alpha}(\bar{\omega})|^2 \]
8. A surprising fact
From the definition of \( \hat{a} \) it can be seen that
\[
\hat{a}(0) = 1 - e^{-\eta(f_1 + \ldots + f_N)} = \mathcal{O}(1)
\]
whereas, for \( \tilde{\omega} \neq 0 \),
\[
\hat{a}(\tilde{\omega})_{\tilde{\omega} \neq 0} = \mathcal{O}\left(\sqrt{N}\right)
\]
The remarkable consequence of this is that for \( \tilde{\omega} = 0 \), that is for \( \omega = \omega_0 \), the pure induced spectrum goes to zero:
\[
S_{II}(\omega = \omega_0) = \lim_{T \to \infty} \frac{1}{T\eta^2} \left|\langle \hat{a}(0) \rangle \right|^2 = 0.
\]

9. Simulations
This system is easy to simulate. Normal deviates can easily be generated, and these give the velocities. As for the intervals between collisions, generating exponentially distributed random variables is easy but it is easier still to use a uniform random number generator on \((0, T)\) to generate \(N\) points. If \(N\) is large enough (and we use 1000 to 10000 points in a run) the distribution is very close to Poisson. We used the Gnu Scientific Library, which has several random number generators, and most of the simulations were run on a laptop. Each run was repeated about 200 times with the same parameters, and the results were averaged.

The figure Fig. 1 below shows the allowed component for one set of parameters \((A = 20, \eta = 0.1)\). Shifting as well as broadening is clearly evident.

![Figure 1. Allowed spectrum, log intensity against \( \tilde{\omega} = \omega - \omega_0 \).](image)

The pure induced component is shown in Figs. 2 and 3 below. It is strongly asymmetric and goes (almost) to zero for \( \tilde{\omega} = 0 \), as predicted. This is much more clearly seen when log intensity is plotted against \( \tilde{\omega} \). For reasons unknown the cross spectrum is small in this example.

We have not endeavoured to obtain the spectra for this model analytically. However, Roger Herman suggested a simplification, in which the phase shift is identically \( \chi \) constant in every collision. The resulting expressions for the components of the spectrum can then be evaluated, and the total spectrum is found to be
\[
S(\omega) = S_{AA}(\omega) + S_{AI}(\omega) + S_{II}(\omega)
= \tilde{\nu}(1 - \cos \eta) \frac{2A^2 + 2A\tilde{\omega}\cos \eta + \tilde{\omega}^2}{4\tilde{\nu}^2 \sin^4 \frac{\eta}{2} + (\tilde{\omega} - \tilde{\nu}\sin \eta)^2}.
\]
A number of changes can be rung on these models but we will leave them for now.
10. Conclusions
The inclusion of phase shifting into the stochastic model drastically modifies the resulting spectra. These become strongly asymmetric, and in fact develop a deep minimum which may actually be zero. However, they not replicate the observed behaviour of actual gas phase HD spectra, though they do seem to resemble the spectra of solid HD. The reasons for this are obscure at present.

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Figure 2. Pure induced spectrum, intensity against $\tilde{\omega} = \omega - \omega_0$.

Figure 3. Pure induced spectrum, log intensity against $\tilde{\omega}$. 