Infilling of Vector Collision–Sequence Interference Dips in Collision–Induced Spectra

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Abstract. The vector interference dip most clearly seen in the fundamental collision–induced band of $\text{H}_2$ and $\text{H}_2$ mixtures at densities upward of 20 amagat, is well known to persist at densities down to 1 amagat. However, at lower densities it is not seen. Lewis and Herman gave a theory of this infilling. In this work we approach the problem from the simple statistical models for collision–induced absorption introduced by Lewis in 2000 and subsequently much elaborated. The statistical model shows infilling, but rather than a uniformly infilling dip the model shows a small central peak forming in the dip, then broadening with increasing amplitude.

1. Introduction
The vector interference dip most clearly seen in the fundamental collision–induced band of $\text{H}_2$ and $\text{H}_2$ mixtures at densities upward of 20 amagat, is well known to persist at densities down to 1 amagat. A. R. W. McKellar noted it at 8 amagat and Bragg et al. [1] found it down to 1 amagat. Indeed, D.H. Rank et al. [2] were able to see the fundamental quadrupole line of $\text{H}_2$ because it sat in an interference dip.

On the other hand the studies of van der Waals complexes of $\text{H}_2$, measured at sub–amagat densities, do not show any such dips [3–5] (note in particular Fig. 1 of ref. [4]). A qualitative explanation appears straightforward: the relevant autocorrelation function is not

\[ \langle \mu(t_1) \cdot \mu(t_2) \rangle \]  \hspace{1cm} (1)

but rather

\[ \langle \mu(t_1) \cdot \mu(t_2) e^{i k \cdot [\vec{x}(t_1) - \vec{x}(t_2)]} \rangle \]  \hspace{1cm} (2)

where $k$ is the wave vector of the incident radiation. The factor

\[ e^{i k \cdot [\vec{x}(t_1) - \vec{x}(t_2)]} \]  \hspace{1cm} (3)

is very close to unity for a smallish molecule, or for collision–induced spectra where the mean free path between collisions is short compared to the wavelength.

However, if the density becomes sufficiently low so that the mean free path is comparable to (actually, rather greater than) the mean free path, the factor (3) becomes in effect a number of modulus 1 and random phase, and on average destroys the negative correlation in the induced dipole moment and so leads to the disappearance of the interference dip.
Lewis and Herman [6] developed a theory of the infilling effect, which predicted that the dip would fill in in a regular fashion, the dip simultaneously becoming shallower and narrower as the ratio of mean free path to wavelength increases (Fig. 1).

It is important to note that there is currently no experimental data showing the infilling of the interference of the dip.

2. The simple statistical models

The simple statistical models of Lewis et al. in their several variations are summarized in ref. [7]. An essential feature is that they suppose instantaneous collisions. Hence the resultant spectra are flat except around the interference dip. The Cartesian components of the velocities are taken from a Gaussian distribution, which for convenience is of zero mean and unit standard deviation. Although cases of zero persistence of velocity are interesting, in this study I usually assume a non–zero persistence, ranging up to 0.99. The velocity series are generated with an AR(1) process [8]:

\[ \mathbf{v}_{j+1} = \varphi \mathbf{v}_j + \mathbf{e}_j \]  

where the \( \mathbf{e}_k \) are independently distributed Gaussian random variables such that each component has zero mean and standard deviation 1. The impulses are given by

\[ f_j = \mathbf{v}_{j+1} - \mathbf{v}_j \]  

and the integrated induced dipole moments are taken proportional to the impulses:

\[ \mu_j = f_j. \]  

The positions \( \mathbf{x}(t_j) \) can be obtained by accumulation:

\[ \mathbf{x}(t_j) = \mathbf{x}(t_{j-1}) + (t_j - t_{j-1}) \mathbf{v}_j. \]  

Then the total integrated induced dipole moment at time \( t \) is given by

\[ M(t) = \sum_j \mu_j \delta(t - t_j) e^{ik\cdot x(t_j)}. \]
The Fourier transform of this is
\[ \mathcal{M}(\omega) = \sum_j \mu_j e^{ik \cdot x(t_j)} e^{-i\omega t_j}. \] (9)

If \( \{t_j\}_j \) is the sequence of collision times lying within \((0, T)\) then
\[ \mathcal{M}(\omega)_T = \sum_{t_j \in (0, T)} \mu_j e^{ik \cdot x(t_j)} e^{-i\omega t_j} \] (10)
is an estimate of the Fourier transform of \( \mathcal{M} \) and the averaged periodogram is
\[ S_T(\omega) = \frac{1}{T} (\mathcal{M}(\omega)_T \cdot \mathcal{M}(\omega)_T^*) . \] (11)

3. Computational approach
We take \( \langle \cdots \rangle \) to mean an average over a large number of sets of collision times \( \{t_j\}_j \) and velocities \( \{v_j\}_j \).

The simulations were carried out in Python 2.7, and made use of the module \texttt{random.py} for the random number generators and the module \texttt{cmath.py} for the complex exponentials. The module \texttt{random.py} uses the Mersenne twister for its basic random number generator.

A total time \( T \) input together with a number of collisions \( N \). Then \( N \) collision times \( t_k \) are chosen by the uniform random number generator to lie within \((0, T)\). \( N \) was always taken to be 16000 in the simulations reported here. \( T \) ranged from 8000 to 209715200.

The calculation of \( S_T \) from eq. (11) for a given parameter set was repeated many times, and the mean taken. For fitting purposes either 5000 or 10000 repetitions were used.

The ratio of the mean free path to the wavenumber \( k \) is
\[ k/\lambda = kN/T \] (12)
as the mean speed is taken to be unity.

The velocity autocorrelation function for velocity in a single direction is
\[ \langle v_x(t) v_x(t + \tau) \rangle = e^{-(1-\varphi)\tau} \] (13)
and so we define an effective mean free path, the distance a particle will travel before being significantly deflected, as
\[ \lambda/(1 - \varphi) . \] (14)

The ratio of the wavenumber \( k \) to this is
\[ \mathcal{R} = k/ [\lambda/(1 - \varphi)] = kN (1 - \varphi) / T \] (15)
and this we use as the independent parameter in our plots.
Figure 2. Infilling of the dip from the simple statistical model. This graph shows results for a series of runs with increasing $k$. Here $\varphi = 0.8$, $N = 16000$ and $T = 8192000$.

Figure 3. Spectrum for an intermediate case. 90000 repetitions were used. At each $\omega$ the mean and one standard deviation on either side of the mean are shown. Here $\varphi = 0.4$, $k = 0.0001$, $N = 16000$ and $T = 98304000$. $\mathcal{R} = 1.024$.

4. Results and analyses

We can analyze such a spectrum as the sum of a Lorentzian dip and a smaller Lorentzian peak:

$$W(\omega) = A \left[1 - \frac{1}{1 + (\omega/w_{dip})^2}\right] + \frac{B}{1 + (\omega/w_{peak})^2}.$$  \hspace{1cm} (16)

As the dip should be a pure Lorentzian, this works well provided that the area of the peak is less than 0.1 of the area of the dip. It is not very good for a spectrum such as that of Fig. 3, which exhibits substantial infilling.

Incorporation of a quartic term in both the dip and the peak gives a much better fit:

$$W(\omega) = A \left[1 - \frac{1}{1 + (\omega/w_{dip})^2 + (\omega/w_{dQ})^4}\right] + \frac{B}{1 + (\omega/w_{peak})^2 + (\omega/w_{pQ})^4}.$$ \hspace{1cm} (17)

The results of this analysis for the above figure are shown below. Both the dip and the peak are slightly broader than their Lorentzian counterparts.
A good way to parametrise the infilling of the dips is by the ratio of the area of the peak to the area of the dip. This ratio lies between 0 and 1. Typical results are shown in Figs. 5 and 6 above. The ratio may depend somewhat on the method of analysis. Use of Lorentzian peaks and dips leads to somewhat smaller numbers for the ratios, but only for cases where the fit residuals indicate poor fits.

Similar graphs are obtained by changing $\varphi$ or changing $k$. However, no scaling which reduces them to a universal curve has been found.
5. Summary
   (i) The interference dips do fill in in this version of the simple statistical models.
   (ii) Rather than fill in uniformly, as per Lewis and Herman, the first infill is a small sharp Lorentzian peak which increases in amplitude and width until the dip is completely filled.
   (iii) The reasons for this behaviour are not totally clear.
   (iv) It is evident by comparing Fig. 1 of ref. [4] with Fig. 1 and Fig. 3 above that the very limited observational data are not sufficient to decide between the two descriptions of the infilling.

References
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