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Elementary Statistical Models for Collision–Sequence Interference Effects with Poisson–distributed Collision Times and Phase Shifting

JOHN COURTENAY LEWIS[1] AND ROGER M. HERMAN[2]

[1]*Department of Physics and Physical Oceanography, Memorial University of Newfoundland, St. John's NL, Canada A1B 3X7*
[2]*104 Davey Laboratory, Department of Physics, Pennsylvania State University, University Park, PA 16802*

ABSTRACT: In this paper the class of model developed for application to collision-sequence interference in refs. [1-3] is extended to include Poisson–distributed collision times and the eects of collisional phase shifting. A key feature is that the velocities are distributed according to a Maxwell–Boltzmann (Gaussian) distribution. Collisions are assumed to be instantaneous, velocities are assumed to be completely randomized in each collision. As applied to scalar collisional interference the models show the presence of a hitherto unknown albeit weak correlation between immediately successive collisions is confirmed.

The addition of a simple model for collisional phase shifting leads to a markedly asymmetric peak, and, most unexpectedly, a zero in the spectrum.

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I. INTRODUCTION

The present work is a continuation of ref. [1], which will henceforth be referred to as ref. I, and of ref. [2], henceforth ref. II. Some parts of the present calculations were summarised in ref. [3]. We also make reference to [4-6] and to [7]. Ref. [8] develops the analogy between scalar interference and Ramsay double resonance. A comprehensive review of the infrared spectra of HD is given by Poll in ref. [9].

At sufficiently low densities and for the study of interference phenomena collisions can be assumed to be instantaneous; the dipole moment induced in one atom or molecule by interaction with a bath of dissimilar atoms or molecules can be represented as

$$\mu(t) = \sum_k \mu_k \delta(t - t_k)\, e^{-\iota\omega_0 t} \tag{1}$$

where binary collision k occurs at time t_k and the dipole moment induced in collision k is μ_k. For the interference dips in Q branches the quantity μ_j is parallel to and approximately proportional in magnitude to the impulse (integrated force) f_k experienced by a molecule in the collision. Our models will be expressed in terms of these impulses f_k. In general the collision times t_k approximate to a Poisson process, and in the present work it will be assumed that they are drawn from a true Poisson process, with frequency $\bar{\nu}$, whereas in ref. [1] the collisions were assumed to occur with at equal intervals.

Eq. (1) describes the transition moment for a transition with frequency ω_0 in the absence of shifting and broadening mechanisms. The resultant spectrum, which shows vector collisional interference, was worked out in ref. II.

II. SCALAR INTERFERENCE

Instead of eq. (1) the scalar modulation of the dipole moment is given by

$$\mu(t)=\left[A+\sum_k \mu_k \delta(t-t_k)\right]e^{\imath\omega_0 t} \tag{2}$$

and its Fourier transform is

$$a_T(\omega)=(A/\tilde{\omega})\left(e^{\imath\tilde{\omega}T}-1\right)+\sum_{t_k\in[0,T]}\mu_k e^{\imath\tilde{\omega}t_k} \tag{3}$$

where we have defined $\tilde{\omega}\equiv\omega-\omega_0$. This we write as $a_T = a_{A,T} + a_{I,T}$ with

$$a_{A,T}(\omega)=(A/\tilde{\omega})\left(e^{\imath\tilde{\omega}T}-1\right) \tag{4}$$

$$a_{I,T}(\omega)=\sum_{t_k\in[0,T)}\mu_k e^{\imath\tilde{\omega}t_k}. \tag{5}$$

The unaveraged periodogram is given by

$$S_T(\omega) = S_{AA,T} + S_{AI,T} + S_{II,T} \tag{6a}$$

$$S_{AA,T}=\frac{1}{T}\left|a_{A,T}\right|^2 \tag{6b}$$

$$S_{AI,T}=\frac{2}{T}\Re e\; a_{A,T}a^*_{I,T} \tag{6c}$$

$$S_{II,T}=\frac{1}{T}\left|a_{I,T}\right|^2. \tag{6d}$$

The allowed contribution to the spectrum then is

$$S_{AA,T}=\frac{1}{\tilde{\omega}^2 T}|A|^2\left(e^{\imath\tilde{\omega}T}-1\right)\left(e^{-\imath\tilde{\omega}T}-1\right)$$

$$=|A|^2\frac{2}{\tilde{\omega}^2 T}(1-\cos\tilde{\omega}T)$$

so the limit as $T\to\infty$ is

$$S_{AA}(\omega)=2\pi|A|^2\,\delta(\tilde{\omega}). \tag{7}$$

The pure induced contribution is given by

$$S_{II,T}=\frac{1}{T}\sum_{k,k'}\mu_k\mu^*_{k'}e^{\imath\tilde{\omega}(t_k-t_{k'})}$$

$$=\frac{1}{T}\sum_k\mu_k\mu^*_k+\frac{2}{T}\Re\mathfrak{e}\sum\mu_k\,\mu^*_{k+1}\,e^{\imath\tilde{\omega}(t_k-t_{k+1})}+\cdots. \tag{8}$$

A principal assumption of the present model, and the feature in which it diers from the class of models discussed in ref. *I*, is that the intervals $\Delta_k\equiv t_{k+1}-t_k$, $k = 1, 2, \ldots, N-1$ between collisions are independent of the velocities of the particle and are exponentially distributed, *i.e.* that the collision times $\cdots t_k, \cdots t_{k'} \cdots$ are random variables which constitute a Poisson process. Poisson–distributed collision times are a good approximation for real gases [10, 11], though not exact.

Assuming Poisson–distributed collision times we find that if $S_{II,T}$ is averaged over an ensemble, and the μ_k are stationary, then eq. (8) becomes

$$S_{II,T}/\bar{\nu} = \left\langle \mu_k \mu_k^* \right\rangle + \frac{2(N-1)}{N} \Re\mathfrak{e} \left\langle \mu_k \mu_{k+1}^* \right\rangle \left\langle \bar{e}^{\imath\tilde{\omega}\Delta_1} \right\rangle$$

$$+ \frac{2(N-2)}{N} \Re\mathfrak{e} \left\langle \mu_k \mu_{k+2}^* \right\rangle \left\langle e^{-\imath\tilde{\omega}(\Delta_1+\Delta_2)} \right\rangle + \cdots. \tag{9}$$

Now if it is assumed, in accord with ref. I, that $\mu_k \propto f_k$, then $\left\langle \mu_k \mu_{k+n}^* \right\rangle = \left\langle \mu_k \right\rangle \left\langle \mu_{k+n}^* \right\rangle = \left| \left\langle \mu_k \right\rangle \right|^2$ for $n > 1$.

If we dene var $f = \langle ff^* \rangle - \langle f \rangle|^2$ then $\left\langle \mu_k \mu_k^* \right\rangle =$ var $\mu_k + |\langle \mu_k \rangle|^2$. Also, cov $(\mu_k, \mu_{k'}^*) \equiv \langle \mu_k, \mu_{k'}^* \rangle - |\langle \mu_l|^2$ and this may be complex. Hence we have $\left\langle \mu_k \mu_{k+1}^* \right\rangle = \mathrm{cov}(\mu_k, \mu_{k+1}^*) + \left| \left\langle \mu_k \right\rangle \right|^2$. Then eq. (9) reduces to

$$S_{II,T}/\bar{\nu} = \mathrm{var}\ \mu + \left| \left\langle \mu \right\rangle \right|^2 + \frac{2(N-1)}{N} \Re\mathfrak{e}\ \mathrm{cov}(\mu_k, \mu_{k+1}^*) \left\langle \bar{e}^{\imath\tilde{\omega}\Delta_1} \right\rangle$$

$$+ \frac{2}{N} \left| \left\langle \mu \right\rangle \right|^2 \Re\mathfrak{e}\ ((N-1) \left\langle e^{-\imath\tilde{\omega}\Delta_1} \right\rangle + (N-2) \left\langle e^{-\imath\tilde{\omega}(\Delta_1+\Delta_2)} \right\rangle + \cdots). \tag{10}$$

If the random variables $\cdots t_k, \cdots, t_{k'}, \cdots$ form a Poisson process then the intervals Δ_i are exponentially distributed [12]:

$$P(\Delta_i) = \bar{\nu} e^{-\bar{\nu}\Delta_i}. \tag{11}$$

The intervals $[0, t_1)$ and $[t_N; T)$ of durations Δ_0 and Δ_N respectively also follow the distribution law (11), this constituting a well–known "paradox" in the theory of Poisson processes.

From eq. (11) it follows immediately that

$$\left\langle e^{-\imath\tilde{\omega}\Delta_1} \right\rangle = \bar{\nu} \int_0^\infty e^{-(\bar{\nu}+\imath\tilde{\omega})\Delta} d\Delta = \frac{\bar{\nu}}{\bar{\nu}+\imath\tilde{\omega}}.$$

In a Poisson process the intervals $\Delta_1, \Delta_2, \cdots$ are independently distributed. Hence eq. (10) is equivalent to

$$S_{II,T}/\bar{\nu} = \mathrm{var}\ \mu + \left| \left\langle \mu \right\rangle \right|^2 + \frac{2(N-1)}{N} \Re\mathfrak{e}\ \mathrm{cov}\left(\mu_k, \mu_{k+1}^* \right) \frac{\bar{\nu}}{\bar{\nu}+\imath\tilde{\omega}}$$

$$+2|\langle \mu \rangle|^2 \Re\mathfrak{e} \left[\left(\frac{N-1}{N} \right) \left(\frac{\bar{\nu}}{\bar{\nu}+\imath\tilde{\omega}} \right) + \left(\frac{N-2}{N} \right) \left(\frac{\bar{\nu}}{\bar{\nu}+\imath\tilde{\omega}} \right)^2 + \cdots \right]$$

$$= \mathrm{var}\ \mu + |\langle \mu \rangle|^2 + \frac{2(N-1)}{N} \Re\mathfrak{e}\ \mathrm{cov}(\mu_k, \mu_{k+1}^*) \frac{\bar{\nu}}{\bar{\nu}+\imath\tilde{\omega}}$$

$$+2|\langle \mu \rangle|^2 \Re\mathfrak{e} \left[\frac{\bar{\nu}^2 - \bar{\nu}^{N+1}(\bar{\nu}+\imath\tilde{\omega})^{1-N} - \imath(N-1)\bar{\nu}\imath\tilde{\omega}}{N\tilde{\omega}^2} \right] \tag{12}$$

Now

$$\lim_{N\to\infty}\mathfrak{Re}\left[\frac{\bar{\nu}^2-\bar{\nu}^{N+1}(\bar{\nu}+\iota\tilde{\omega})^{1-N}-\iota(N-1)\bar{\nu}\,\iota\tilde{\omega}}{N\tilde{\omega}^2}\right]=\bar{\nu}\pi\delta(\tilde{\omega})$$

so that, in the limit $T\to\infty$, $N/T=\bar{\nu}$ =const, eq. (12) becomes

$$S_{II}(\omega)/\bar{\nu}=\mathrm{var}\,\mu+|\langle\mu\rangle|^2+2(\mathfrak{Re}\;\mathrm{cov}(\mu_k,\mu^*_{k+1}))\frac{\bar{\nu}^2}{\bar{\nu}^2+\tilde{\omega}^2}$$

$$+2(\mathfrak{Im}\;\mathrm{cov}(\mu_k,\mu^*_{k+1}))\frac{\bar{\nu}\tilde{\omega}}{\bar{\nu}^2+\tilde{\omega}^2}+2\pi\bar{\nu}|\langle\mu\rangle|^2\,\delta(\tilde{\omega}). \tag{13}$$

If $\mu_k \propto f_k$ this implies that $\mu_k/f_k = const$, where *const* is a constant independent of k. This being the case, $\mu_k\mu^*_{k+1}$ is real and $\mathfrak{Im}$ cov $(\mu_k,\mu^*_{k+1})=0.$ Hence eq. (13) becomes

$$S_{II}(\omega)/\bar{\nu}=\mathrm{var}\,\mu+|\langle\mu\rangle|^2+2\,\mathrm{cov}(\mu_k,\mu^*_{k+1})\frac{\bar{\nu}^2}{\bar{\nu}^2+\tilde{\omega}^2}+2\pi\bar{\nu}|\langle\mu\rangle|^2\,\delta(\tilde{\omega}). \tag{14}$$

In ref. I it was found that cov $(f_k, f_{k+1})\neq 0$ for the models under discussion, this being independent of the form of the distribution of collision times used. Hence eq. (14) predicts that, in addition to the constant background var μ + $|\langle\mu\rangle|^2$, which becomes the observed broad peak for collisions which are not instantaneous, and the sharp interference peak $2\pi\bar{\nu}|\langle\mu\rangle|^2\,\delta(\tilde{\omega}),$ there is a positive feature with Lorentzian shape and HWHH of $\bar{\nu}$ and maximum given by 2 cov (μ_k,μ^*_{k+1}).

III. INCLUSION OF PHASE SHIFTING IN SCALAR INTERFERENCE

During a collision the frequency of oscillation of the molecule shifts; or, in more vigorous collisions, a nonradiative transition may take place, a possibility which can be ignored for simple models of the hydrogens. The effect is that during a collision k the phase of the oscillation increases from $-\iota\omega_0 t$ to $-\iota\omega_0 t-\iota\eta_k$. This phase shift results in broadening and shifting of the resultant spectral line, and also gives the induced dipole moment real and imaginary parts, which in turn leads to line shapes of dispersion form [13, 14]. The molecular processes involved have been discussed at length by Tabisz *et al.* [15–19] and by Gustafsson and Frommhold [20, 21].

In the spirit of the models being developed herein, we will assume that the shift in phase induced in a collision k is given by $\eta_f=\eta[\boldsymbol{f}k]$, i.e. we assert that η_f is a functional of the impulse $\boldsymbol{f}k$. We will often use the simple approximation $\eta_f=\eta f_k$ where η is a parameter. Then the time dependence of the allowed part of the induced dipole moment modulation is given by

$$\mu_A(t)=\mathrm{A}e^{-\omega_0 t-\iota\eta\varphi(t)} \tag{15a}$$

$$\varphi(t)=\sum_{k=1}^{N} f_k h(t-t_k) \tag{15b}$$

where h is a Heaviside step function:

$$h(t-t_k)=\begin{cases}0 & for\, t<t_k,\\ 1 & for\, t>t_k\\ 1/2 & for\, t=t_k.\end{cases} \tag{16}$$

The induced part of the scalar modulation, when phase shifting is included [14], is

$$\mu_I(t) = \sum_{k=1}^{N} f_k \delta(t - t_k) e^{-\iota\omega_0 t - \iota\eta\varphi(t)}. \tag{17}$$

Then the total scalar modulation of the dipole moment becomes

$$\mu(t) = \left[A + \sum_{k=1}^{N} f_k \delta(t - t_k) \right] e^{-\iota\omega_0 t - \iota\eta\varphi(t)} \tag{18}$$

instead of (2). The Fourier transform of $\mu(t)$ over $[0, T)$ we denote, as above, by $aT(\omega)$. The contribution to a_T coming from the allowed part of $\mu(t)$ in eq. (18) is given by

$$a_{A,T}(\omega)/A = \int_0^T dt\, e^{\iota\omega t} e^{-\iota\omega_0 t - \iota\eta\varphi(t)} \tag{19}$$

$$\begin{aligned} &= \int_0^{t_1} dt\, e^{\iota\tilde{\omega}t} + e^{-\iota\eta f_1} \int_{t_1}^{t_2} dt\, e^{\iota\tilde{\omega}t} + e^{-\iota\eta(f_1+f_2)} \int_{t_2}^{t_3} dt\, e^{\iota\tilde{\omega}t} + \cdots \\ &\quad + e^{-\iota\eta(f_1+\ldots+f_{N-1})} \int_{t_{N-1}}^{t_N} dt\, e^{\iota\tilde{\omega}t} + e^{-\iota\eta(f_1+\ldots+f_N)} \int_{t_N}^{T} dt\, e^{\iota\tilde{\omega}t} \end{aligned} \tag{20}$$

whence

$$(\iota\tilde{\omega}/A) a_{A,T}(\omega) = \tilde{a}(\tilde{\omega}) \tag{21}$$

with

$$\begin{aligned} \tilde{a}(\tilde{\omega}) &= \left(e^{\iota\tilde{\omega}t_1 - 1}\right) + e^{-\iota\eta f_1}\left(e^{\iota\tilde{\omega}t_2} - e^{\iota\tilde{\omega}t_1}\right) + e^{-\iota\eta(f_1+f_2)}\left(e^{\iota\tilde{\omega}t_3} - e^{\iota\tilde{\omega}t_2}\right) + \ldots \\ &\quad + e^{-\iota\eta(f_1+\ldots+f_{N-1})}\left(e^{\iota\tilde{\omega}t_N} - e^{\iota\tilde{\omega}t_{N-1}}\right) + e^{-\iota\eta(f_1+\ldots+f_N)}\left(e^{\iota\tilde{\omega}T} - e^{\iota\tilde{\omega}t_N}\right). \end{aligned} \tag{22}$$

For the induced part we have

$$\mu_I(t) = e^{-\iota\omega_0 t - \iota\eta\varphi(t)} \sum_k f_k\, \delta(t - t_k) \tag{23a}$$

$$= e^{-\iota\omega_0 t} \left(\frac{\iota}{\eta}\right) \frac{d}{dt} e^{-\iota\eta\varphi(t)}. \tag{23b}$$

Its Fourier transform is

$$\begin{aligned} a_{I,T}(\omega) &= \int_0^T dt\, e^{\iota\omega t} \mu_I(t) \\ &= \int_0^T dt\, e^{\iota\omega t}\, e^{-\iota\omega_0 t - \iota\eta\,\varphi(t)} \sum_k f_k\, \delta(t - t_k) \\ &= \left(\frac{\iota}{\eta}\right) \int_0^T dt\; e^{\iota\tilde{\omega}t} \frac{d}{dt} e^{-\iota\eta\varphi(t)} \\ &= \left(\frac{\iota}{\eta}\right) \left[e^{\iota\tilde{\omega}t} e^{-\iota\eta\varphi(t)} \right]_0^T + \frac{\tilde{\omega}}{\eta} \int_0^T dt\; e^{\iota\tilde{\omega}t} e^{-\iota\eta\varphi(t)} \end{aligned} \tag{24a}$$

$$= \left(\frac{\iota}{\eta}\right)\left[e^{\iota\tilde{\omega}T-\iota\eta(f_1+...+f_N)}-1\right]+\frac{\tilde{\omega}}{\eta}(a_{A,T}(\tilde{\omega})/A) \tag{24b}$$

where $a_{A,T}\ (\tilde{\omega})$ is given by eqs. (19) through (22).

Hence, using eq. (22) we nd that

$$\begin{aligned} a_{I,T}\ (\tilde{\omega}) &= -\frac{\iota}{\eta}\hat{a}(\tilde{\omega}) \\ \hat{a}(\tilde{\omega}) &= e^{\iota\tilde{\omega}t_1}+e^{-\iota\eta f_1}\left(e^{\iota\tilde{\omega}t_2}-e^{\iota\tilde{\omega}t_1}\right)+e^{-\iota\eta(f_1+f_2)}\left(e^{\iota\tilde{\omega}t_3}-e^{\iota\tilde{\omega}t_2}\right)+... \\ &\quad +e^{-\iota\eta(f_1+...+f_{N-1})}\left(e^{\iota\tilde{\omega}t_N}-e^{\iota\tilde{\omega}t_{N-1}}\right)-e^{-\iota\eta(f_1+...+f_N)}e^{\iota\tilde{\omega}t_N} \qquad (25a) \\ &= e^{\iota\tilde{\omega}t_1}(1-e^{-\iota\eta f_1})+e^{-\iota\eta f_1}e^{\iota\tilde{\omega}t_2}(1-e^{-\iota\eta f_2})+e^{-\iota\eta(f_1+f_2)}e^{\iota\tilde{\omega}t_3}(1-e^{-\iota\eta f_3}) \\ &\quad +\cdots+e^{-\iota\eta(f_1+\cdots f_{N-1})}e^{\iota\tilde{\omega}t_N}(1-e^{-\iota\eta f_N}). \end{aligned}$$

The manipulations in eqs. (23) and (24) involve combinations of δ–functions and Heaviside functions, which are not quite standard. However, if the δ–functions are replaced with sharply peaked regular functions such as $\Delta\ (u,\ \epsilon)$ = exp $[-u^2/2\epsilon^2]/\sqrt{2\epsilon})]$ and the Heaviside functions are replaced with the corresponding smoothed step functions $H\ (u,\ \epsilon)$ = [1 + Erf $(u\ /\ \sqrt{2\epsilon}$)] / 2 the manipulations can be veried. Taking $\epsilon \to 0$ recovers the δ and Heaviside functions. The matter is further discussed in App. A.

Indeed, it is plausible that R an expression for $a_{I,T}$ alternative to eq. (25c) might be obtained by integrating $\int_0^T dt\, e^{\iota\omega t}\ \mu_I(t)$ directly, to obtain

$$\begin{aligned} a_{I,T}(\omega) &= \int_0^T dt\, e^{\iota\omega t}\ \mu_I(t) \\ &= \sum_k f_k\, e^{\iota\tilde{\omega}t_k}e^{-i\eta\varphi_k} \end{aligned} \tag{26}$$

where φ_k is dened as

$$\varphi_k \equiv \varphi(t_k) = \sum_{j=1}^{k-1} f_j + \frac{1}{2}f_k \tag{27}$$

as a consequence of eq. (16). However, eq. (26) is incorrect: it does not agree with eq. (25c), though the differences for impulses f_k of 1 or 2 and for $|\eta| \le 0.2$ are at most a few percent (see App. B). The situation is reminiscent of the Ito–Stratonovich dilemma (for which see van Kampen [22]) but in the present situation it is clear that eq. (25c) rather than eq. (26) is the correct expression for the Fourier transform of $\mu(t)$.

In sum, the Fourier transform of $\mu(t)$ on [0, T) is given by

$$a_T(\omega) = a_{A,T}(\omega) + a_{I,T}(\omega) \tag{28a}$$

$$= A\frac{\tilde{a}(\tilde{\omega})}{\iota\tilde{\omega}} - \frac{\iota}{\eta}\hat{a}(\tilde{\omega}). \tag{28b}$$

The unaveraged periodogram is, therefore,

$$S_T(\omega) \equiv \frac{1}{T}|\,a_T(\omega)\,|^2 \tag{29a}$$

$$=\frac{1}{T}|A|^2\frac{|\tilde{a}(\tilde{\omega})|^2}{\tilde{\omega}^2}+\frac{2}{T_\eta}\mathfrak{Re}\ A\frac{\hat{a}(\tilde{\omega})\,\tilde{a}(\tilde{\omega})^*}{\tilde{\omega}}+\frac{1}{T\eta^2}|\hat{a}(\tilde{\omega})|^2\,. \tag{29b}$$

The pure allowed contribution is

$$S_{AA,T}(\omega)=\frac{1}{T}|A|^2\,\frac{|\tilde{a}(\tilde{\omega})|^2}{\tilde{\omega}^2}. \tag{30}$$

The pure induced contribution is

$$S_{II,T}(\omega)=\frac{1}{T\eta^2}|\hat{a}(\tilde{\omega})|^2\,. \tag{31}$$

The cross term is

$$S_{AI,T}(\omega)=\frac{2}{T\eta}\mathfrak{Re}\ A\frac{\hat{a}(\tilde{\omega})\,\tilde{a}(\tilde{\omega})^*}{\tilde{\omega}}. \tag{32}$$

(A) A Remarkable Property of $\hat{a}(\tilde{\omega})$

From eq. (25b) it can be seen that

$$\hat{a}(0)=1-e^{-\iota\eta(f_1+\ldots+f_N)}=\mathcal{O}(1) \tag{33}$$

whereas, for $\tilde{\omega}\neq 0$, the series in eq. (25b) describes a random walk; hence

$$\hat{a}(\tilde{\omega})_{\tilde{\omega}\neq 0}=\mathcal{O}(\sqrt{N}). \tag{34}$$

The remarkable consequence of this is that for $\tilde{\omega}=0$, that is for $\omega=\omega_0$, the pure induced spectrum goes to zero:

$$S_{II}(\omega=\omega_0)=\lim_{T\to 0}\frac{1}{T\eta^2}\left\langle|\hat{a}(0)|^2\right\rangle=0. \tag{35}$$

Now from eq. (25c)

$$\begin{aligned}\hat{a}'(0)&=t_1(1-e^{-\iota\eta f_1})+t_2\,e^{-\iota\eta f_1}(1-e^{-\iota\eta f_2})+t_3e^{-\iota\eta(f_1+f_2)}(1-e^{-\iota\eta f_3})\\&\quad+\ldots+t_N\,e^{-\iota\eta(f_1+\ldots+f_{N-1})}(1-e^{-\iota\eta f_N})=\mathcal{O}(\sqrt{N})\end{aligned} \tag{36}$$

so that

$$S_{II}(\omega)\propto\tilde{\omega}^2 \tag{37}$$

for suciently small $\tilde{\omega}$.

It had been thought that the known asymmetric line profiles found in scalar interference were due to a complex modulation function μ_k. However, we have shown that a real modulation function $\mu_k=f_k$ will lead to an asymmetric profiles.

IV. CONCLUSIONS

In the rest part of this paper it is determined that the weak correlation found in paper I in scalar interference does lead to a Lorentzian spectral feature with hwhh equal to the mean collision frequency if a Poisson process is used for the collision times.

In the second part of the paper, a shifting mechanism is introduced, in which the shift of the emission frequency during a collision is taken to be proportional to the impulse f_k undergone by the molecule during the collision.

For the allowed contribution to the line shape we obtain a Lorentzian prole: the shifting and broadening operates essentially according to Lindholm's theory [23]. For the pure induced contribution, however, the result is very surprising: the profile is asymmetric, and indeed if the shifting is assumed to be exactly proportional to the impulse f_k then we have shown that the pure induced spectrum goes to zero at the unperturbed frequency of the molecular transition.

Analytic evaluation of the expressions above when phase shifts are included is difficult. However, it is straightforward to simulate (18). The results of these simulations will be discussed in a subsequent paper.

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APPENDIX A: PROOF OF AN EXPRESSION FOR THE FOURIER TRANSFORM OF THE INDUCED PART OF THE SCALAR MODULATION

In this appendix we will examine the derivation of eq. (25c) from eq. (17).

1. Continuum Approach

We wish to evaluate

$$a(\tilde{\omega}) = \int_{\epsilon_1}^{\epsilon_2} f\,\delta(t-\tau) e^{\iota\tilde{\omega}t} e^{-\iota\eta f h(t-\tau)} dt, \quad \tau \in (\epsilon_1, \epsilon_2) \tag{A1}$$

where h is the Heaviside unit step function. We note that

$$f\,\delta(t-\tau) e^{-\iota\eta f h(t-\tau)} = \frac{-1}{\iota\eta} \frac{\partial}{\partial t} e^{-\iota\eta f h(t-\tau)} \tag{A2}$$

whence (A1) is equivalent to

$$\begin{aligned} a(\tilde{\omega}) &= \int_{\epsilon_1}^{\epsilon_2} f\,\delta(t-\tau) e^{\iota\tilde{\omega}t} e^{-\iota\eta f h(t-\tau)} dt \\ &= \frac{\iota}{\eta} \int_{\epsilon_1}^{\epsilon_2} e^{\iota\tilde{\omega}t} \frac{\partial}{\partial t} e^{-\iota\eta f h(t-\tau)} dt \\ &= \frac{\iota}{\eta} \left\{ \left[e^{\iota\tilde{\omega}t} e^{-\iota\eta f h(t-\tau)} \right]_{\epsilon_1}^{\epsilon_1} - \int_{\epsilon_1}^{\epsilon_2} e^{-\iota\eta f h(t-\tau)} \frac{\partial}{\partial t} e^{\iota\tilde{\omega}t} dt \right\} \\ &= \frac{\iota}{\eta} \left\{ e^{\iota\tilde{\omega}\epsilon_2} e^{-\iota\eta f} - e^{\iota\tilde{\omega}\epsilon_1} - \iota\tilde{\omega} \int_{\epsilon_1}^{\epsilon_2} e^{-\iota\eta f h(t-\tau)} dt \right\}. \end{aligned} \tag{A3}$$

Now

$$\begin{aligned} \int_{\epsilon_1}^{\epsilon_2} e^{\iota\tilde{\omega}t} e^{-\iota\eta f h(t-\tau)} dt &= \int_{\epsilon_1}^{\tau} e^{\iota\tilde{\omega}t} e^{-\iota\eta f h(t-\tau)} dt + \int_{\tau}^{\epsilon_2} e^{\iota\tilde{\omega}t} e^{-\iota\eta f h(t-\tau)} dt \\ &= \int_{\epsilon_1}^{\tau} e^{\iota\tilde{\omega}t} dt + \int_{\tau}^{\epsilon_2} e^{\iota\tilde{\omega}t} e^{-\iota\eta f} dt \end{aligned}$$

$$= \frac{1}{\iota\tilde{\omega}}\left[e^{\iota\tilde{\omega}t}\right]_{\epsilon_1}^{\tau} + \frac{1}{\iota\tilde{\omega}}\left[e^{\iota\tilde{\omega}t}e^{-\iota\eta f}\right]_{\tau}^{\epsilon_2}$$

$$= \frac{1}{\iota\tilde{\omega}}\left\{e^{\iota\tilde{\omega}\tau} - e^{\iota\tilde{\omega}\epsilon_1} + e^{\iota\tilde{\omega}\epsilon_2}e^{-\iota\eta f} - e^{\iota\tilde{\omega}\tau}e^{-\iota\eta f}\right\}. \tag{A4}$$

Substitution of eq. (A4) into eq. (A3) yields

$$a(\tilde{\omega}) = \frac{1}{\iota\eta}e^{\iota\tilde{\omega}\tau}(1 - e^{-\iota\eta f}). \tag{A5}$$

Eq. (25c) can be obtained by taking $\tau = t_1, t_2, \ldots, t_N$ successively in eq. (24a) and superposing the results.

2. An Analytical Approach using a Sequence Approximating to δ

Another approach is to use a sequence of functions for the δ function chosen so that the Fourier transform can be obtained analytically. One such set of functions is

$$\Delta(x,\epsilon) = \begin{cases} 0 & |x| \geq \epsilon \\ \dfrac{1}{2\epsilon} & -\epsilon < x < \epsilon \end{cases} \tag{A6}$$

with the smoothed step function

$$H(x,\epsilon) = \int_{-\infty}^{x} \Delta(x',\epsilon)dx' = \begin{cases} 0 & x \leq -\epsilon \\ \dfrac{x+\epsilon}{2\epsilon} & -\epsilon < x < \epsilon \\ 1 & x \geq \epsilon. \end{cases} \tag{A7}$$

For these approximations to the delta function and the Heaviside function we have

$$a(\tilde{\omega},\epsilon) = \int_{-\infty}^{\infty} f\Delta(t-\tau,\epsilon)e^{\iota\tilde{\omega}t}e^{-\iota\eta f H(t-\tau,\epsilon)}dt$$

$$= -\frac{\iota e^{\iota\tau\tilde{\omega}}(e^{-\iota\epsilon\tilde{\omega}} - e^{-\iota\eta f + \iota\epsilon\tilde{\omega}})}{\eta - 2\epsilon\tilde{\omega}} \tag{A8}$$

and

$$\lim_{\epsilon\to 0} a(\tilde{\omega},\epsilon) = -\frac{\iota e^{\iota\tau\tilde{\omega}}(1 - e^{-\iota\eta f})}{\eta} \tag{A9}$$

in agreement with eq. (A5) above.

APPENDIX B: COMPARISON OF TWO EXPRESSIONS FOR THE FOURIER TRANSFORM OF THE INDUCED PART OF THE SCALAR MODULATION

As discussed in section (III) above, there are two apparently plausible expressions for the Fourier transform of the pure induced scalar modulation $\mu(t)$. The first such expression for a single collision time τ is given by eq. (A5) above. The alternative expression is, from eq. (26), given by

$$a_i(\tilde{\omega}) = f\, e^{\iota\tilde{\omega}\tau} e^{-\iota\eta f/2}. \tag{B1}$$

Expanding $a(\tilde{\omega})$ in η we obtain

$$a(\tilde{\omega}) = f - \frac{1}{2}\iota f^2\eta - \frac{f^3\eta^2}{6} + \frac{1}{24}\iota f^4\eta^3 + O[\eta]^4 \tag{B2}$$

while expanding $a_i(\tilde{\omega})$ yields

$$a_i(\tilde{\omega}) = f - \frac{1}{2}\iota f^2\eta - \frac{f^3\eta^2}{8} + \frac{1}{48}\iota f^4\eta^3 + O[\eta]^4; \tag{B3}$$

the dierence is

$$a(\tilde{\omega}) - a_i(\tilde{\omega}) = -\frac{f^3\eta^2}{24} + \frac{1}{48}\iota f^4\eta^3 + O[\eta]^4. \tag{B4}$$

Comparison of eqs. (25c) and eq. (26) for simulations carried out with $\eta = 0.2$ and with $\eta = 0.1$ for several thousands of collision times gives agreement within at worst about 6%.

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