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The Line Shape for Collisionally Broadened Molecular Transitions: A Quantum Theory Satisfying the Fluctuation Dissipation Theorem

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to be consistent with an analysis of the water vapor continuum.

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The Line Shape for Collisionally Broadened Molecular Transitions: A Quantum Theory Satisfying the Fluctuation Dissipation Theorem

1. INTRODUCTION

The dipole autocorrelation function for spectral line broadening is treated in a quantum theory which rigorously satisfies the fluctuation dissipation theorem^{1,2} on a microscopic level. The basic approximation in the theory is the binary collision approximation. The two-body interaction is decomposed into a part which commutes with the internal coordinates of both the radiator and the perturber, and a part which does not. The theory, as developed, is appropriate for broadening mechanisms for which the non-commuting terms may be treated within the framework of perturbation theory, while the commuting term is to be treated exactly. The theory gives, at long times, a result for the dipole autocorrelation function consistent with the well-known impact approximation. At short times, an autocorrelation function of Gaussian form, with a renormalization of the initial state occupancy is obtained. It is found that the qualitative features discussed above are unaltered in higher order perturbation theory. The results are consistent with the requirement that all time derivatives of the autocorrelation function at $t = 0$ exist. This further satisfies the requirement that all moments of the lineshape function in the frequency domain exist, hence that the lineshape function decays "exponentially"

(Received for publication 24 September 1982)

1. Callen, H. B., and Welton, T. A. (1951) Phys. Rev. 83:34.
2. Kubo, R. (1959) in Lectures in Theoretical Physics Vol. I, Eds., Brittin, W. E., and Dunham, L. G., Interscience Pub., Inc., N. Y., p. 120.

sufficiently far in the wings. The computational procedure for obtaining the spectral line shape from the present theory within the framework of the uncoupled line approximation will be discussed. A more extensive development of the theory has been given by Davies et al.³

2. THEORY

The absorption coefficient, $\alpha(\omega)$, for an ensemble of molecules is given by

$$\alpha(\omega) = \frac{4\pi^2}{3hc} \omega \chi''(\omega) \quad (1)$$

where ω is the frequency and $\chi''(\omega)$ is the imaginary part of the complex susceptibility. The quantity, $\chi''(\omega)$, may be expressed in terms of the Fourier transform of an appropriate dipole moment autocorrelation function, $\phi(t)$. There are three generally used forms for this description of $\chi''(\omega)$:

$$\chi''(\omega) = \frac{1 - e^{-\beta\hbar\omega}}{1 + e^{-\beta\hbar\omega}} \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} [\phi(t) + \phi(-t)], \quad (2a)$$

$$\chi''(\omega) = (1 - e^{-\beta\hbar\omega}) \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \phi(t), \quad (2b)$$

and

$$\chi''(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} [\phi(t) - \phi(-t)], \quad (2c)$$

where $\beta = (kT)^{-1}$. The equivalence of these three expressions is established by satisfying the fluctuation-dissipation theorem^{1,2} (FDT).

In the frequency domain, the statement of the fluctuation-dissipation theorem is expressed by

$$\phi(-\omega) = e^{-\beta\hbar\omega} \phi(\omega), \quad (3a)$$

which, in the time domain, implies

$$\phi(-t) = \phi(t + i\beta\hbar), \quad (3b)$$

3. Davis, R. W., Tipping, R. H., and Clough, S. A. (1982) Phys. Rev. A26:3378.

where

$$\phi(\omega) = \int_{-\infty}^{\infty} dt e^{-i\omega t} \phi(t). \quad (4)$$

In order to gain insight into the influence of the fluctuation-dissipation theorem on the line shape, it is instructive to consider the effect of the failure to satisfy the FDT on the far wing of a spectral line. Consider the impact result for the auto-correlation function,

$$\phi(t) \Rightarrow \sum_{if} \rho_i |\mu_{if}|^2 e^{-\gamma_{fi}|t|} e^{i\omega_{fi}t}, \quad (5a)$$

with spectral density

$$\Phi(\omega) \Rightarrow \sum_{if} \rho_i |\mu_{if}|^2 \frac{1}{\pi} \left[\frac{\gamma_{fi}}{\gamma_{fi}^2 + (\omega - \omega_{fi})^2} \right] \quad (5b)$$

where ρ_i is the diagonal element of the density matrix, μ_{if} is the transition moment describing a transition from the i to f state, γ_{fi} is a parameter (the halfwidth) descriptive of the Markovian collision process, and ω_{fi} ($\hbar\omega_{fi} = \epsilon_f - \epsilon_i$) is the transition frequency (which for simplicity includes any shift term). The impact result for $\phi(t)$ clearly does not satisfy FDT since $\phi(-t) \neq \phi(t + i\hbar)$. The three expressions for the imaginary part of the susceptibility become

$$\chi_1''(\omega) = \frac{1 - e^{-\beta\hbar\omega}}{1 + e^{-\beta\hbar\omega}} \sum_{if} \rho_i |\mu_{if}|^2 \frac{1}{\pi} \left[\frac{\gamma_{fi}}{\gamma_{fi}^2 + (\omega - \omega_{fi})^2} + \frac{\gamma_{fi}}{\gamma_{fi}^2 + (\omega + \omega_{fi})^2} \right] \quad (6a)$$

$$\chi_2''(\omega) = (1 - e^{-\beta\hbar\omega}) \sum_{if} \rho_i |\mu_{if}|^2 \frac{1}{\pi} \left[\frac{\gamma_{fi}}{\gamma_{fi}^2 + (\omega - \omega_{fi})^2} \right] \quad (6b)$$

$$\chi_3''(\omega) = \sum_{if} \rho_i |\mu_{if}|^2 \frac{1}{\pi} \left[\frac{\gamma_{fi}}{\gamma_{fi}^2 + (\omega - \omega_{fi})^2} - \frac{\gamma_{fi}}{\gamma_{fi}^2 + (\omega + \omega_{fi})^2} \right]. \quad (6c)$$

These three impact line shapes are generally referred to as the Van Vleck-Weisskopf, the simple Lorentz, and the full Lorentz respectively, although the front dependence on $\beta\hbar\omega$ is often not correctly given. If we consider the blue wings for which $\beta\hbar\omega \gg 1$ and $\omega \gg \omega_{fi}$, we obtain

$$\chi_1''(\omega) = \sum_{if} \rho_i |\mu_{if}|^2 \frac{1}{\pi} \frac{\gamma_{fi}}{\omega^2} \quad (2) \quad (7a)$$

$$\chi_2''(\omega) = \sum_{if} \rho_i |\mu_{if}|^2 \frac{1}{\pi} \frac{\gamma_{fi}}{\omega^2} \quad (1) \quad \text{and} \quad (7b)$$

$$\chi_3''(\omega) = \sum_{if} \rho_i |\mu_{if}|^2 \frac{1}{\pi} \frac{\gamma_{fi}}{\omega^2} \left(\frac{4\omega_{fi}}{\omega} \right). \quad (7c)$$

This clearly demonstrates that an autocorrelation function which does not satisfy the FDT, for example, the impact autocorrelation function, gives significantly different results for the far line wing using these three different formulations. Additionally, it should be noted, that the impact autocorrelation function does not satisfy another important condition: the function is not analytic at $t = 0$ and as a consequence the higher order moments in the frequency domain are not finite.

An example of the type of problem for which the present discussion has direct relevance is the continuum absorption observed in the self broadened water vapor spectrum.^{4,5} The symmetrized spectral density function, $\langle \phi(\omega) + \phi(-\omega) \rangle$, for this case is shown in Figure 1. The water vapor continuum, $\langle \phi(\omega) + \phi(-\omega) \rangle_{\text{cont}}$, utilized in this computation is indicated by the dotted line and is obtained from a line by line calculation from which the contribution within 25 cm^{-1} of the line center has been excluded. The line shape is taken as the product of the impact line profile, Eq. (5b), with an exponential type function containing three parameters adjusted to attain agreement with the continuum observations. The continuum based on this profile provides good agreement with experiment in the entire spectral region from $0\text{-}5000 \text{ cm}^{-1}$, including the three atmospheric "windows", $0\text{-}10 \text{ cm}^{-1}$, $950\text{-}1250 \text{ cm}^{-1}$, and $2000\text{-}2500 \text{ cm}^{-1}$ as shown in Figure 2. For comparison, we show the continuum resulting from the impact line shape alone as indicated by the dashed line and observe that $\langle \phi(\omega) + \phi(-\omega) \rangle_{\text{cont}}$ is too large in the window regions and too small in regions of strong absorption. It is clear from these results that only a proper description of the collisional broadening will resolve the issue of the role of line shape vis-à-vis other mechanisms in contributing to the continuum absorption in these spectral regions. A critical test of the theoretical results will be the extent to which the theory describes the strong temperature dependence of the observed continuum absorption in the 1000 cm^{-1} and 2500 cm^{-1} regions.⁵

4. Clough, S.A., Kneizys, F.X., Davies, R.W., Gamache, R., and Tipping, R.H., (1980) in *Atmospheric Water Vapor* edited by Deepak, A., Wilkerson, T.D., Rhunke, L.H., Academic, Press, New York, p. 25.

5. Burch, D.E. (1981) *Continuum Absorption by H₂O*, AFGL-TR-81-0300, AD A112264 (available from NTIS).

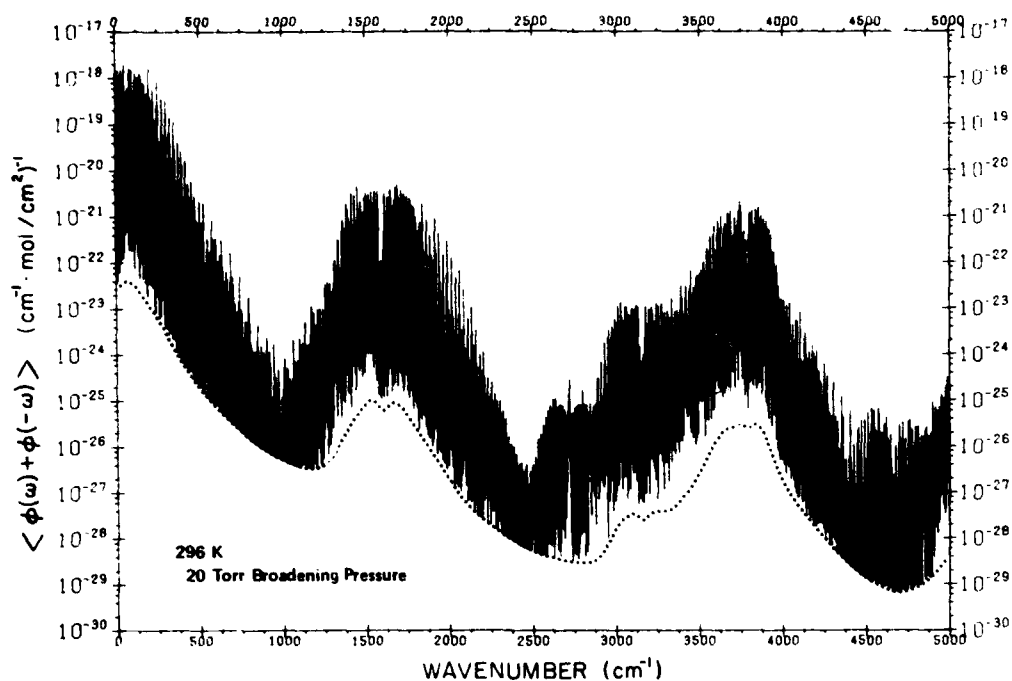


Figure 1. Power Spectral Density, $\langle \phi(\omega) + \phi(-\omega) \rangle$, Self Broadened Water Vapor. The continuum (...) is obtained using a modified impact line shape (see text)

The objective of the present theoretical development is to obtain an autocorrelation function which satisfies the FDT, treats the physics of collisions and is computationally tractable. The Hamiltonian for the entire system may be separated into two parts.

$$H = H_0 + V \quad (8)$$

in which H_0 describes the unperturbed molecular energies including intermolecular interactions commutative with the internal coordinates of the radiator (including the dipole moment operator $\bar{\mu}$) and the perturber, and V is the non-commutative part of the interaction potential. The matrix elements of V will be obtained in a representation in which H_0 is assumed to have been solved exactly, that is, in which realistic quantum mechanical trajectories have been obtained. The theory is developed assuming the binary collision and the uncoupled line approximations. The final results involve a second order perturbative treatment of the potential V .

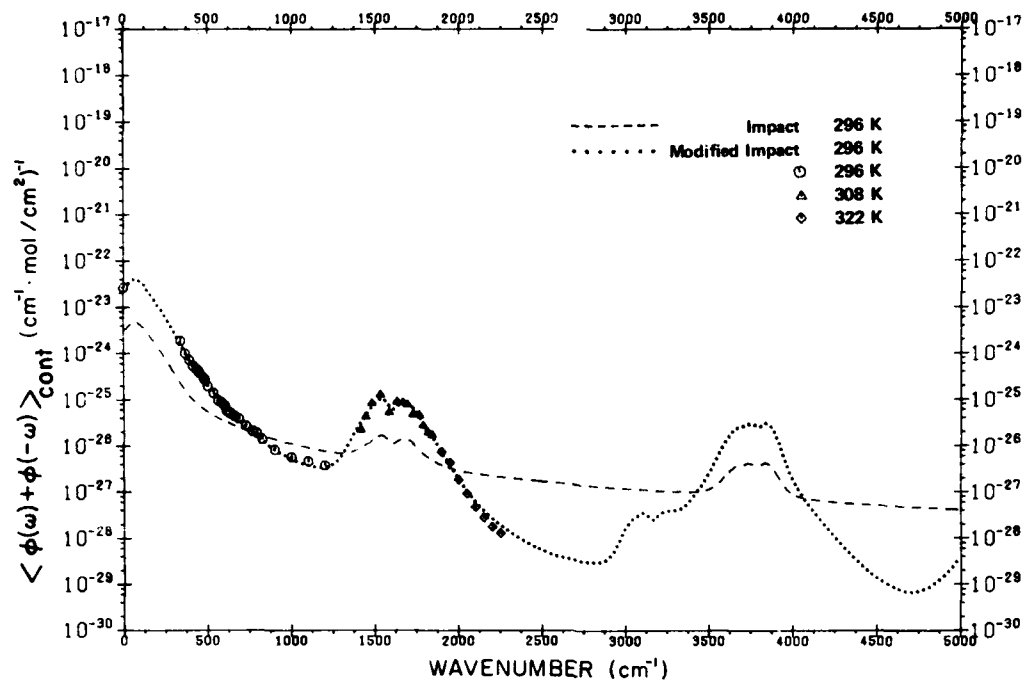


Figure 2. Power Spectral Density, $\langle \phi(\omega) + \phi(-\omega) \rangle_{\text{cont}}$, for the Self Broadened Water Vapor Continuum. Experimental data is from Burch, Reference 5

We start with the definition for the dipole moment autocorrelation function for the system, $\phi(t)$,

$$\phi(t) = \text{Tr} [\bar{\mu}(0) \cdot \bar{\mu}(t) \rho(H)], \quad (9)$$

where $\rho(H)$ is the canonical density operator, and $\bar{\mu}(0)$ is the dipole moment operator. For $\bar{\mu}(t)$ given by the Heisenberg operator

$$\bar{\mu}(t) = e^{iHt/\hbar} \bar{\mu}(0) e^{-iHt/\hbar} \quad (10)$$

and $\rho(H)$ by

$$\rho(H) = e^{-\beta H} / Z \quad (11)$$

with Z the partition sum, we obtain for $\phi(t)$,

$$\rho(t) = Z^{-1} \text{Tr} [\bar{\rho}(0) \cdot e^{iHt/\hbar} \bar{\rho}(0) e^{-iH(t-i\beta\hbar)/\hbar}] . \quad (12)$$

Defining a time development operator, $U(t)$ through the relation

$$e^{-iHt/\hbar} = e^{-iH_0 t/\hbar} U(t) \quad (13)$$

and similarly for complex time, $t-i\beta\hbar$,

$$e^{-iH(t-i\beta\hbar)/\hbar} = e^{-iH_0 t/\hbar - \beta H_0} U(t-i\beta\hbar) \quad (14)$$

we obtain

$$\rho(t) = \frac{Z_0}{Z} \text{Tr} [\bar{\rho}(0) \cdot U(t)^\dagger e^{iH_0 t/\hbar} \bar{\rho}(0) e^{-iH_0 t/\hbar} \rho(H_0) U(t-i\beta\hbar)] . \quad (15)$$

At this stage of the development, we sum over the internal radiator states, designated i and f , suppressing the explicit m dependence for simplicity of presentation. We also make the uncoupled line approximation, although this approximation could be delayed until a later stage, and obtain the result

$$\rho(t) = \frac{Z_0}{Z} \sum_{if} \rho_i \mu_{if}^2 C_{if}(t) e^{i\omega_{fi} t} \quad (16)$$

where

$$C_{if}(t) = \text{Tr} [\rho(\tilde{H}_0) U_{ii}(t-i\beta\hbar) U_{ff}(t)^\dagger] . \quad (17)$$

Here \tilde{H}_0 designates that part of H_0 not dependent on internal radiator coordinates and thus the trace operation is to be taken over the internal perturber states and the translational states.

The binary collision approximation assumes that the correlation function for the system, $C_{if}(t)$, is expressible as a product of correlation coefficients, $c_{if}(t)$, which characterize an individual radiator-perturber pair,

$$C_{if}(t) = [c_{if}(t)]^{N_p} \quad (18)$$

where N_p is the number of perturbers and

$$c_{if}(t) = \text{Tr} [\rho^S(\tilde{H}_0) U_{ii}^S(t-i\beta\hbar) U_{ff}^S(t)^\dagger] . \quad (19)$$

The superscript s denotes that the system now consists of a single radiator and a single perturber. Following Baranger,⁶ we assume that $c_{if}^s(t)$ may be written in the form

$$c_{if}^s(t) = 1 + \frac{n_p}{N_p} a_{if}^s(t) \quad (20)$$

where n_p is the perturber number density and the ratio n_p/N_p is associated with the normalization volume. In the limit of large N_p we obtain

$$C_{if}^s(t) = \left[c_{if}^s(t) \right]^{N_p} = \left[1 + \frac{n_p}{N_p} a_{if}^s(t) \right]^{N_p} \approx e^{n_p a_{if}^s(t)}. \quad (21)$$

Thus

$$C_{if}^s(t) = e^{N_p [c_{if}^s(t) - 1]} \quad (22)$$

and on substituting Eq. (19) we obtain

$$C_{if}^s(t) = \exp \left\{ N_p \left\{ \text{Tr} [\rho^s(\tilde{H}_0) U_{ii}^s(t-i\beta\hbar) c_{ff}^s(t)] - 1 \right\} \right\}. \quad (23)$$

The time development operator may be written in the following integral form:

$$U^s(t) = 1 - W^s(t), \quad (24)$$

where

$$W^s(t) = \frac{i}{\hbar} \int_0^t V^s(t') U^s(t') dt', \quad (25)$$

thus $C_{if}^s(t)$ becomes

$$C_{if}^s(t) = \exp \left\{ - N_p \left\{ \text{Tr} \left[\rho^s(\tilde{H}_0) W_{ii}^s(t-i\beta\hbar) \right] + \text{Tr} \left[\rho^s(\tilde{H}_0) W_{ff}^s(t) \right] - \text{Tr} \left[\rho^s(\tilde{H}_0) W_{ii}^s(t-i\beta\hbar) W_{ff}^s(t) \right] \right\} \right\}. \quad (26)$$

6. Baranger, M. (1958) Phys. Rev. 112:855.

It proves convenient to define the operator $K_f(t)$,

$$K_f(t) = \text{Tr} \left[\rho^s(H_0) W_{ff}^s(t)^\dagger \right] \quad (27)$$

and similarly the operators K_i and K_{if} so that $C_{if}(t)$ is expressible as

$$C_{if}(t) = \exp \left\{ -N_p [K_i(t-i\beta\hbar) + K_f(t) - K_{if}(t, t-i\beta\hbar)] \right\} \quad (28)$$

and $\phi(t)$ as

$$\phi(t) = Z^{-1} \sum_{if} \rho_i \mu_{if}^2 e^{i\omega_{fi}t} \exp \left\{ -N_p [K_i(t-i\beta\hbar) + K_f(t) - K_{if}(t, t-i\beta\hbar)] \right\} \quad (29)$$

where we have suppressed the superscript s . This result may be considered rigorous within the binary collision and uncoupled line approximations.

The evaluation of $\phi(t)$ as given by Eq. (29) remains a formidable problem. At this stage we use second order perturbation theory but caution that the procedure is valid only if the matrix elements of the interaction potential V are small in the representation in which H_0 is diagonal. We proceed by evaluating $K_f(t)$ through second order and obtain

$$K_f(t) = \int_0^\infty dk \rho_k \int_0^\infty dk' \left(\sum_{\ell\ell'} V_{k\ell k'\ell'}^2 \right) \sum_{f'} \mu_{ff'}^2 \sum_j \rho_j \sum_{j'} \mu_{jj'}^2 f_{\alpha\beta}(t). \quad (30)$$

The time dependence is contained in the function $f_{\alpha\beta}(t)$,

$$f_{\alpha\beta}(t) = \frac{1}{\omega_{\alpha\beta}} \left[(1 - \cos \omega_{\alpha\beta}t) - i(\omega_{\alpha\beta}t - \sin \omega_{\alpha\beta}t) \right], \quad (31)$$

with

$$\omega_{\alpha\beta} = \epsilon_f - \epsilon_{f'} + \epsilon_j - \epsilon_{j'} + \epsilon_k - \epsilon_{k'}. \quad (32)$$

The matrix elements, $V_{k\ell k'\ell'}$, are obtained in the representation in which H_0 is diagonal, that is, the representation diagonal in the internal states of the radiator, the internal states of the perturber and the translational states for the isotropic potential, $V_0(R)$. For the dipole-dipole interaction appropriate to self-broadened water vapor problem, we have with angular integrations and m sums suppressed,

$$V_{k\ell k'\ell'} = \langle \psi_{k\ell}(R) | \frac{\hat{\mu}_r \cdot \hat{\mu}_p - \hat{\mu}_r \cdot \hat{R} \hat{\mu}_p \cdot \hat{R}}{R^3} | \psi_{k'\ell'}(R) \rangle \quad (33)$$

where $\hat{\mu}_r$ and $\hat{\mu}_p$ are unit vectors associated with the dipole moment of the radiator and perturber respectively, and R is the intermolecular distance. The wavefunction, $\psi_{k\ell}(R)$, associated with translational energy ϵ_k is obtained from the solution of the Schrodinger equation for the collisional problem,

$$\left\{ -\frac{\hbar^2}{2M} \nabla^2 + V_0(R) + \frac{\hbar^2}{2M} \frac{\ell(\ell+1)}{R^2} \right\} \psi_{k\ell}(R) = \epsilon_k \psi_{k\ell}(R). \quad (34)$$

We now investigate the long and short time behavior of $K_f(t)$ given by the function $f(t)$. Making use of the identities

$$\lim_{t \rightarrow \infty} \frac{1 - \cos \omega_{\alpha\beta} t}{\omega_{\alpha\beta}} = |t| \pi \delta(\omega_{\alpha\beta}) \quad (35a)$$

and

$$\lim_{t \rightarrow \infty} \frac{\omega_{\alpha\beta} t - \sin \omega_{\alpha\beta} t}{\omega_{\alpha\beta}} = t \text{Pr} \left(\frac{1}{\omega_{\alpha\beta}} \right) \quad (35b)$$

with Pr denoting the principal value, we can obtain the long time behavior of $K_f(t)$. For the real part we have

$$\text{Re } K_f(t) \propto |t| \int_0^\infty dk \rho_k \int_0^\infty dk' \sum_{\ell\ell'} V_{k\ell k'\ell'}^2 \sum_{f'} \mu_{ff'}^2 \sum_j \rho_j \sum_{j'} \mu_{jj'}^2 \pi \delta(\omega_{\alpha\beta}) \quad (36)$$

and for the imaginary part,

$$\text{Im } K_f(t) \propto t \int_0^\infty dk \rho_k \int_0^\infty dk' \sum_{\ell\ell'} V_{k\ell k'\ell'}^2 \sum_{f'} \mu_{ff'}^2 \sum_j \rho_j \sum_{j'} \mu_{jj'}^2 \text{Pr} \left(\frac{1}{\omega_{\alpha\beta}} \right). \quad (37)$$

This result for long times is consistent with the time dependence obtained from other formulations of the impact result from second order perturbation theory;⁷ specifically the real part associated with the width varies as $|t|$ and the imaginary part associated with the shift varies as t .

7. Anderson, P. W. (1949) Phys. Rev. 76:647.

For small times, the behavior of $K_f(t)$ may be obtained by expanding $f(t)$, and in the limit as $t \rightarrow 0$, we obtain

$$K_f(t) \approx \mu_r^2 \mu_p^2 t^2 \int_0^\infty dk \rho_k \int_0^\infty dk' \sum_{\ell \ell'} V_{k \ell k' \ell'} t^2. \quad (38)$$

In the small time regime, $K_f(t)$ is a real quadratic function of time, whereas $K_f(t-i\beta\hbar)$ contains a contribution from the FDT; for dipole-dipole interactions, K_{if} vanishes.³ The real part of the correlation function in this limit is, nevertheless, of Gaussian form.

In order to provide additional insight into the functional form of the dipole moment autocorrelation function, $\phi(t)$, it is useful to consider a reference function having an analytic Fourier transform. We choose as a convenient reference the complex function, $G(t)$, for which

$$\text{Re } G(t) = a_0 \left\{ e^{-a_1 t^2} \otimes e^{-a_2 |t|} \right\} \quad (39a)$$

and

$$\text{Im } G(t) = b_0 \left\{ t e^{-b_1 t^2} \otimes e^{-b_2 |t|} \right\}. \quad (39b)$$

The symbol \otimes denotes the convolution operation. It should be noted that a_0 is chosen such that $\text{Re } G(0) = 1$ and a_1 and a_2 are chosen to fit the short and long time behavior of $\text{Re } \phi(t)$, Eq. (29). Similarly, for $\text{Im } \phi(t)$, b_0 and b_2 are chosen to fit the short and long time behavior of $\text{Im } \phi(t)$, and b_1 is assumed equal to a_1 .

Having defined the reference function, we now consider the difference, $\Delta(t)$, between the dipole autocorrelation function, $\phi(t)$, and the reference function $G(t)$,

$$\Delta(t) = \phi(t) - G(t). \quad (40)$$

This procedure has two purposes: To allow consideration of the results of the current theory on a scale which is manageable, and to facilitate the computation of the Fourier transform for the resultant line shape. To illustrate the functional properties of the autocorrelation function, we plot in Figure 3 a typical $\Delta(t)$ calculated from an approximate $\phi(t)$ that has the qualitatively correct time dependence. For a more complete calculation of $\phi(t)$ we expect the oscillations to be less pronounced with the convergence to the impact limit ($\text{Re}\Delta(t)=0$) to occur more smoothly and at a shorter time. The rapid variation at the short time limit is expected to remain, reflecting the collision dynamics on the time scale commensurate with the duration of collision.

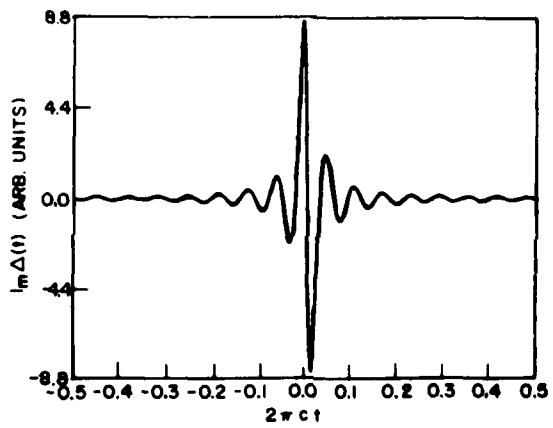
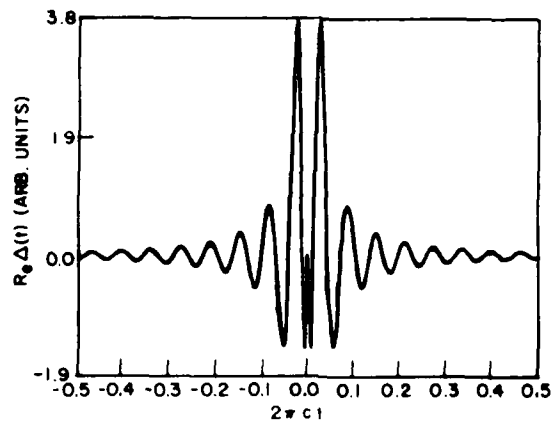


Figure 3. Real and Imaginary Parts of the Difference Function, $\Delta(t)$, Calculated From an Approximate $\phi(t)$

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