KALAHARI JOURNALS

International Review of Atomic and Molecular Physics
Vol. 4 No. 2 (December, 2018)

REVIEW ARTICLE

INTRA-COLLISION EFFECTS IN THE COLLISION-BROADENING OF SPECTRAL LINE PROFILES

GEORGE C. TABISZ*
Department of Physics and Astronomy, University of Manitoba, Winnipeg, Manitoba, Canada, R3T 0C2

Received: 13rd August 2017 Revised: 24th December 2017 Accepted: 10th March 2018

Abstract: Some details of events occurring during collisions that affect the profiles of collision-broadened spectral lines are reviewed. Emphasis is on the impact and quasi-static approximations. Rotational level mixing and collisional propagation are shown to be important processes. The general principles are illustrated through consideration of the infrared spectrum of the hydrogen molecule.

Collision-broadened spectral line shapes carry important information on the time-dependent dynamical and collisional processes occurring in the radiating medium. The physical description involves the dynamical evolution of the radiator as it undergoes a series of multiple collisions with a large number of perturbers, while the interaction between the radiator dipole moment and the external electromagnetic field results in absorption and emission processes.

This article reviews, in an informal manner, a particular aspect of collisional broadening, namely some details of what can transpire during the collisions that are ultimately responsible for the broadening phenomenon. Both allowed and collision-induced electric-dipole transitions are treated. The material is not new but consideration of these phenomena within a single context provides insight into their character. The infrared spectrum of the hydrogen molecule provides an ideal illustration of some of the general phenomena involved.

1. COMMON APPROXIMATIONS

To begin, recall some basic principles employed in the consideration of allowed transitions. Many treatments of collisional line broadening are presented within the impact approximation (or limit) where the time between collisions controls the spectral line width. This approximation is often taken to mean that the time of duration of collisions may be considered small compared to the time between collisions, thereby rendering the details of what happens during the collision unimportant. This last statement can mislead. More correctly, and mathematically, the approximation applies in the regime where[1]

$$(\omega-\omega_0)\tau_C << 1 \qquad \text{... (1)}$$

Here $(\omega-\omega_0)$ is the detuning from the line centre at ω_0 and τ_C is the time duration of the collision. The major part of this paper concerns the situation where the collision does indeed have a finite duration and, moreover, where collisional propagation, i.e. inelastic transitions occurring during the collision process, but not due to radiative processes, are prominent. Only the modifications to the shape and intensity of the profile are discussed; the more subtle changes in frequency shift are not considered.

The work of Boulet, Robert, Galatry and Marteau[2, 3] provides an introduction to the concept. The absorption coefficient at frequency ω is given by:

$$\alpha(\omega) = n_R\left(\frac{4\pi}{3\hbar c}\right)\omega\left[1-\exp\left(-\frac{\hbar\omega}{kT}\right)\right]\phi(\omega), \qquad \text{... (2)}$$

where

$$\phi(\omega) = \frac{1}{\pi}\Re e\int_0^\infty \exp(-i\omega t)C(t) \qquad \text{... (3)}$$

and

---

* *E-mail: tabisz@shaw.ca, tabisz@cc.umanitoba.ca*

$$C(t) = <\vec{\mu}(0) \bullet \vec{\mu}(t)> \qquad \text{... (4)}$$

is the autocorrelation function of the dipole moment operator $\vec{\mu}(t)$. $C(t)$ can be represented as:

$$C(t) = \exp(i\omega_0 t)\exp\left(-n_p\sigma^3\psi(t)\right) \qquad \text{... (5)}$$

where n_R and n_p are the number densities of the radiators and of the perturbers respectively, σ is the collision diameter specified by the intermolecular potential, and $\psi(t)$ is a dimensionless function. In the impact approximation, a linear dependence of $\psi(t)$ on t is obtained for times longer than the collision duration time (typically, a fraction of a picosecond). The Fourier transform of $C(t)$ is a Lorentzian profile. The slopes of the straight lines of the real and imaginary parts of $n_p\sigma^3\psi(t)$ versus t respectively give the halfwidth γ and frequency shift δ of the spectral profile (Fig. 1).

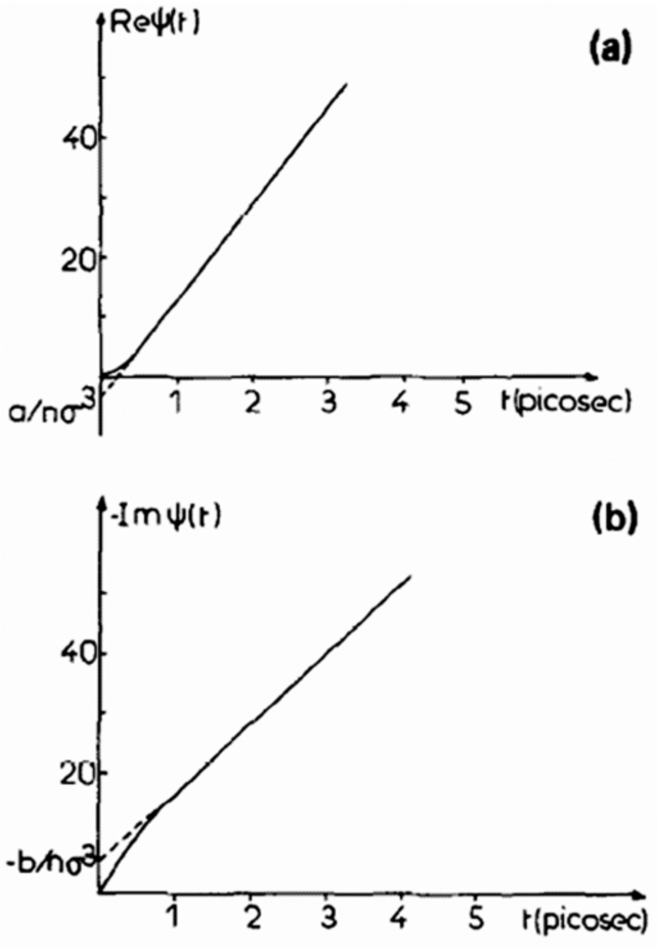

Fig. 1: Calculated values of the ψ (t) function for the HF-Ar R (2) line in the 0-2 band at 295 K. In the notation of the present paper the vertical axes in this figure are (a) $P/n_p\sigma^3$ and (b) $-Q/n_p\sigma^3$ (reprinted with permission from Ph. Marteau, C. Boulet and D. Robert, J. Chem. Phys. 80, 3632 (1984). Copyright 1984, American Institute of Physics.)

These lines however, do not necessarily pass through the origin. The asymptotic behaviour for $t \geq \tau_C$ may be expressed as:

$$\lim_{t>>\tau_C} n_p\sigma^3\psi(t) = (\gamma + i\delta)t + P + iQ \qquad \text{... (6)}$$

The quantities P and Q characterize the effect of the finite duration of collision on the line shape. In the core region of the profile for moderate densities where $(\omega - \omega_0 - \delta) << \tau_C^{-1}$ and $\gamma << \tau_C^{-1}$, the profile is the sum of a Lorentzian and an anomalous dispersion line shape whose amplitudes are modified by a factor $\exp(-P/\pi\gamma)$, i.e.

$$\phi(\omega) = \frac{\exp(-P)}{\pi\gamma}\left[\frac{\gamma^2}{\gamma^2 + (\omega - \omega_0 - \delta)^2} + \frac{Q\gamma(\omega - \omega_0 - \delta)}{\gamma^2 + (\omega - \omega_0 - \delta)^2}\right] \qquad \text{... (7)}$$

The total line shape is thus asymmetric with intensity modified from that obtained from the pure impact approximation.

$\psi(t)$ is usually obtained by two separate approaches. For times much greater than τ_C, the impact limit is adequate. For times smaller than τ_C, the quasi-static approximation gives accurate results. In it the perturbers are thought to be stationary during the collision and their motion neglected. Again more correctly, this regime is characterized by a mathematical relationship[1]

$$(\omega - \omega_0)\tau_C >> 1 \qquad \text{... (8)}$$

It is thus often appropriate to treat long range collision in the impact approximation and short-range collisions in the quasi-static limit.

These two limiting approaches can be reconciled through a unified theory that provides a representation of $\psi(t)$, which includes the intermediate region lying between the quasi-static and impact regimes.[4]

Now consider not just solely allowed transitions but a more general case where both allowed and collision-induced transitions may be present. Collision-induced transitions occur quite generally and are due to dipoles induced in pairs or higher order clusters of molecules or atoms through molecular or atomic interactions. The induced dipole moment by its nature is a short-lived entity, in effect, existing only during the duration of the collision. The dipoles and their associated spectra are weak in magnitude and intensity respectively and are usually observed in highly symmetric systems where allowed transitions are forbidden.[5,6]

For example, the symmetric molecule H_2 does not have a permanent dipole moment in the ground electric state nor an allowed infrared spectrum. It does, however, display a collision-induced pure rotational and vibrational- rotational spectrum that has been extensively studied.[5,6] The hydrogen isotopomer HD does have a small permanent dipole moments of the order of 10^{-3} to 10^{-4} D which lies along the direction of its interatomic axis.[7,8] This moment is responsible for allowed rotational and vibrational transitions in the HD spectrum. The formalism outlined in the following may be applied judiciously to both H_2 and HD.

2. A GENERAL FORMALISM

Consider a system consisting of a single diatomic molecule (absorber or radiator) immersed in a bath of perturbers, here taken to be neutral atoms.[9] The whole system lies in an electromagnetic radiation field. The molecule has a series of low-lying energy levels that are to be taken as vibration-rotation levels. The perturbers have much more widely spaced energy levels, taken as electronic energy levels, Electric dipole allowed transitions are assumed possible between levels in the radiator and perturbers. In addition interactions between the molecule and the perturbers induce cluster electric dipole moments that may also participate in radiative transitions at several frequencies, including the same frequencies as the allowed transitions. Then it is possible that the probability amplitudes for an allowed and induced transition interfere.[10−13] Absorption and stimulated emission events as considered. Radiative lifetimes of excited states are long compared to the duartion of a collision τ_C and the time between collisions. Spontaneous emission is therefore ignored. The spacing of the molecular states is not large compared to $\hbar / \tau_C$ or kT. As a result the radiator-perturber interaction may cause mixing and inelastic collisions among the molecular states. The radiator is assumed to be at rest (heavy radiator approximation) and the perturbers are considered to move along classical trajectories.

To treat this system, the density matrix of the gas in which collisions take place is constructed and its evolution in the presence of the incident radiation is described to obtain the absorption and stimulated emission spectrum.[9] There are several contributions to the absorption coefficient which arise from different physical phenomena. Four of them are immediately relevant to the present discussion, namely:

$$\alpha(\omega) = \left(\frac{4\pi}{3\hbar c}\right)\omega \times$$

$$\lim_{s\to 0} 2\Re e \left(Tr_R \left\{ \begin{array}{l} n_R\left[\mathsf{L}(\omega)\right]^{-1}\hat{D}_R\Sigma^B\hat{D}_R^{*} \\ -n_R n_p\left[\mathsf{L}(\omega)\right]^{-1}(L_R+i\omega) \\ \qquad \left[\int_0^\infty e^{(L_R+i\omega)\tau-s\tau}\left\langle \begin{matrix} U_e^I(\tau,0)\hat{D}_e^I(0) \\ U_e^I(0,-\infty) \end{matrix}\right\rangle_{av} d\tau\right]\Sigma^B\hat{D}_R^{*} \\ -n_R n_p\left[\int_0^\infty \left\langle \hat{D}_e^{I\downarrow}(0)U_e^I(0,-\tau)\right\rangle_{av} e^{(L_R+i\omega)\tau-s\tau}d\tau\right] \\ \qquad (L_R+i\omega)\left[\mathsf{L}(\omega)\right]^{-1}\hat{D}_R\Sigma^B \\ +n_R n_p\left[\int_0^\infty \left\langle \begin{matrix} \hat{D}_e^{I\downarrow}(\tau)U_e^I(\tau,0) \\ \hat{D}_e^I(0,-\infty) \end{matrix}\right\rangle_{av} e^{i\omega\tau-s\tau}d\tau\right]\Sigma^B \end{array} \right\} \right) \quad \ldots (9)$$

These equations are written in the Liouville space formalism.[14] U_e^I is the one-perturber collisional propagation operator in the interaction picture and is a Liouville space operator; $\hat{D}_e^I$ is the induced dipole moment in the interaction picture and is a Hilbert space operator; $\hat{D}_R$ is the allowed dipole moment of the molecular operator and also is a Hilbert space operator; Σ^B is the Boltzmann distribution function for the molecular states. The superscript ↓ denotes a Hermitian conjugate. Each of these terms will be elucidated in the following paragraphs. The details of the derivation of this expression need not concern us here; they may be found in ref. 9.

The first term describes the purely allowed spectrum. Here n_R is the number density of the molecular radiators. Transitions occur between the initial state g and an excited state e. The second and third terms describe interference between the amplitudes for allowed and collision-induced transitions. Again n_p is the perturber number density; L_R is the Liouville operator associated with the Hamiltonian of the free molecular radiator. The average (av) indicated by the angular brackets is taken over all the collision variables (velocity, impact parameter, orientation). The last term describes collision-induced transitions occurring in a single collision and is the principal contributor to the purely collision-induced spectrum. Intercollisional interference effects in the purely collision-induced spectrum are neglected in the present discussion.

The line shape operator $\mathsf{L}(\omega)$ appears in the first three terms and is given by

$$L(\omega) = -(L_R + i\omega) + n_p\left[\int_0^\infty \left\langle V_e^{aI}(0) U_e^{I}(0,-\tau)\right\rangle_{av} e^{(L_R+i\omega)\tau - s\tau} d\tau\right] (L_R + i\omega) \qquad \text{... (10)}$$

V_e^{aI} is the Liouville operator associated with the anisotropic part of the interaction potential and is written in the interaction picture. The presence of the line shape operator in the interference terms means that the spectral features to which they give rise have similar width and shifts to that of the purely allowed lines. The last term depends solely on propagation during the collision and its width thus depends on the duration of the collision.

In what follows, it is important to be aware of two important and related phenomena. One is rotational level or line mixing that arises because of the presence of anisotropic components in the intermolecular potential. The other is the collisional propagation among rotational levels that is due to inelastic collisions during the finite duration of the collision.

3. THE INTERFERENCE TERMS

Even if the purely allowed and the interference terms are evaluated in the impact approximation, collisional propagation is still present. For example consider a transition between an initial state $|g\rangle$ and a final state $|e\rangle$. After a translation of the time origin from 0 to t_0 in the second term, the history of the system, as described by it, may be presented as follows. The molecule starts in an arbitrary state $|J_i\rangle$ at $t = -\infty$ and the system propagates to $t = t_0$ while the molecule possibly undergoes J or m mixing. At $t = t_0$ there is an interaction with the light field through the induced dipole moment in general connecting two intermediate J_m states of the molecule, $|2\rangle$ and $|3\rangle$. The system then propagates to the end of the collision. At $t = +\infty$ there remains a coherence between $|J_e m_e\rangle$ and $|J_g m_g\rangle$. This is path 1 in Fig. 2. Then the molecule interacts with the light field through the allowed dipole moment to leave the molecule in state $|J_e\rangle$. This is path 2 in Fig. 2. Interference occurs between the quantum mechanical amplitudes associated with these two paths. The mixing effect is important if $(\omega_{eg} - \omega_{32})\tau_C \le 1$. The time t_0 represents the time between the radiative event and the time of closest approach.

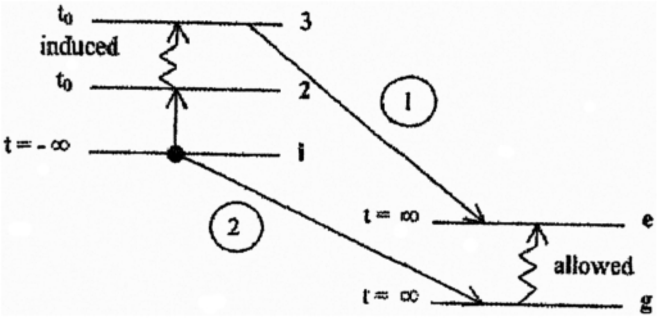

Fig. 2: The pathways contributing to interference between allowed and induced transitions as described by the second term in Eq. (9). The zigzag arrows denote radiative transitions and the straight arrows represent collisional propagation and mixing. (reprinted from G.C. Tabisz, in weakly interacting molecular pairs: unconventional absorbers of radiation in the atmosphere, Edited by C. Camy-Peyret and A. A. Vigasin, (Kluwer, Dordrecht, 2003), pp. 83. Copyright Kluwer, 2003)

The third term describes a process in which the allowed radiator dipole initially creates a $|J_e\rangle\langle J_g|$ coherence and the system propagates to $t = t_0$ with the radiator possibly undergoing J and m mixing. At $t = t_0$ the induced dipole acts leaving the radiator in an arbitrary state $|J_3\rangle$. Again interference can occur between the amplitudes for these two paths. Again the mixing is important if $(\omega_{eg} - \omega_{32})\tau_C \le 1$.

When the impact approximation is made, the total absorption coefficient may be parameterized as the sum of Lorentzian and anomalous dispersion components and the expression for the total absorption coefficient due to these three terms is:

$$\alpha(\omega) = \rho_R\left(\frac{4\pi\omega}{3\hbar c}\right)\left(1 - \exp\left(-\frac{\hbar\omega}{kT}\right)\right)\sum_{J_g}{}^{B}\left|\mu_R\right|^2 \times\left(\frac{B\rho_p/\pi}{(\omega-\omega_0-S\rho_p)^2+(B\rho_p)^2}\left(1+a\rho_p+b\rho_p{}^2\right) - \frac{(\omega-\omega_0-S\rho_p)/\pi}{(\omega-\omega_0-S\rho_p)^2+(B\rho_p)^2}\left(c\rho_p+d\rho_p{}^2\right)\right) \qquad \text{... (11)}$$

Here ρ_R and ρ_p are the radiator and perturber densities in amagat units, $\sum_{J_g}^{B}$ is the Boltzmann function for state J_g, and μ_R is the reduced matrix element of the allowed radiator dipole. The parameter B is a line-broadening coefficient and S is a frequency shift coefficient. The four parameters *a*, *b*, *c* and *d* describe the role of the interference process in the absorption process; *a* and *c* refer to effects which occur in single collisions as described above. The leading interference parameter *a* affects the strength of the symmetric Lorentzian component and *c* controls the asymmetry of the total profile. The parameters *b* and *d* play roles analogous to the latter two, but for effects important at high densities and happening in successive collisions. They arise from additional terms appearing in Eq. (9) which have been excluded here for purposes of clarity and brevity.[9] All four parameters depend on the permanent dipole moment of the molecule and on the pair induced moment.

Such interference effects have only been observed in systems involving HD[10, 11, 15–19]. In general, coherence, which is a necessary ingredient for the occurrence of interference, is a manifestation of indistinguishability. In the HD problem, the amplitudes of two electric dipole transitions between the same initial and final states are capable of interference, despite vastly different origins. In the simplest scenario, both the small magnitude and symmetry properties of its permanent moment are the crucial factors that permit observable interference to occur. References 11 – 13 provide an elaboration of this mechanism.

The treatment discussed here goes beyond that simplest scenario.[9] The parameters *B*, *a*, *b*, *c* and *d* appearing in Eq. (11) have been evaluated by the taking of the collision average through the computer simulation of the molecule-perturber interaction.[20–24] The HD-Ar and HD-He systems have been treated. Both semi-empirical anisotropic interaction potentials (V_e) and *ab initio* calculations of the induced dipole moment (D_e) are available from the literature. The results demonstrate that inelastic collisions are indeed crucial.

Calculations have been made both with semi-classical trajectories[20–23] and through a fully quantum mechanical approach.[24] The following describes some typical results. First consider the pure rotational spectrum in the infrared region (Fig. 3).

The R_0 (*J*) lines are allowed but also contain contributions from the interference terms. For the broadening coefficient *B* (Table 1) the semi-classical calculations can differ with experiment by up to a factor of 2 and the one available fully quantum result (ref. 24) agrees well with experiment. Clearly the cases where only elastic collisions were used cannot account the observed broadening.

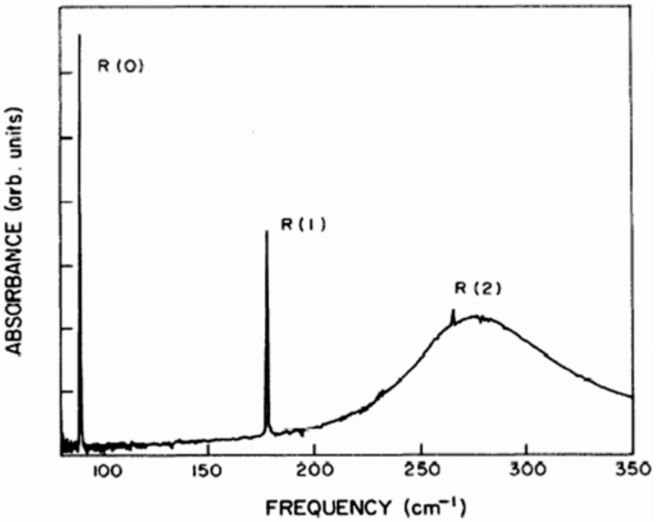

Fig. 3: The far infrared absorbance spectrum of pure HD at 42.8 amagats and 77 K. The sharp R (J) lines (more correctly, R_0 (J)) sit upon a broad collision-induced background. (reprinted with permission from L. Ulivi, Z. Lu and G.C. Tabisz, Phys. Rev. A 40, 62 (1989). Copyright 1989, The American Physical Society)

Table 1
Broadening coefficient, *B*, cm^{-1} amagat^{-1}. Results are from Ref. 21 unless otherwise specified

	Temperature (K)		*Experiment*	*Full Calc.*	*Elastic Coll. Only*
		HD-He			
R_0(0)	77		0.15	0.31 0.18 [24]	3.7 × 10^{-2}
R_0(2)	195		0.41	0.48	1.2 × 10^{-6}
		HD-Ar			
R_0(0)	195		1.4	2.2	1.3
R_0(1)	295		1.5	2.3	4.4 × 10^{-3}

For the interference parameter *a*, there are large differences between calculations permitting inelastic collisions and those that do not (Table 2). In particular a pronounced *J*-dependence appears for the former case. For the asymmetry parameter *c* the same tends are evident (Table 3). Notice that experimentally its sign may change from line to line and that the calculation is capable of providing agreement.

Similar calculations have been made for the R_1 (*J*) lines of the vibration-rotation transitions.[22,23] In this case, collisional propagation can occur in principle among rotational levels in the ground vibrational state, among levels in the excited vibrational state and between levels in these two vibrational states. Collision duration is too long and experimental temperatures normally too low to make the last contribution significant and it is neglected in this analysis. The parameters *a* and *c* depend on $(\mu_R)^{-1}$ and *b* and *d* on $(\mu_R)^{-2}$. The allowed transition dipole μ_R is about -8.3×10^{-4} *D* for pure rotational transitions and $+5.5 \times 10^{-5}$ *D* for lines in the fundamental band. The parameters *a* and *c* should then differ by a factor of about -15 between the two types of transitions and *b* and *d* by about 230. In fact *a* and *c* are always of opposite sign and *b* and *d* are almost always of the same sign (as expected). The ratio of these magnitudes however, can be considerably different from 15 and 230. (For details concerning these results the reader is asked consult references 21 to 24). Collisional propagation in the excited vibrational state is thereby shown to be important. Comparison with experiment is only possible for $R_1(0)$ and $R_1(1)$ at 77 K. Agreement is good for *a* and reasonable for *b*; *c* and *d* on the other hand are too small. The calculation, semi-classical or quantum mechanical, does not predict as large an asymmetry as observed.

Table 2
Interference parameter, *a*, 10^{-3} amagat^{-1}. Results are from Ref. 21 unless otherwise specified

	Temperature (K)	*Experiment*	*Full Calc.*	*Elastic Coll. Only.*
	HD-He			
$R_0(0)$	77	6.0 (16)	2.99	4.33
$R_0(2)$	77	4.4 (15)	6.47	4.34
$R_1(0)$	77	−1.44 (2) [16]	−1.83 [23]	
	HD-Ar			
$R_0(1)$	295	1.8 (3)	3.22	8.92
$R_0(2)$	295	6.1 (2)	7.80	8.92

Table 3
Asymmetry parameter, *c*, 10^{-3} amagat^{-1}. Results are from Ref. 21 unless otherwise specified

	Temperature (K)	*Experiment*	*Full Calc.*	*Elastic Coll. Only*
	HD-He			
$R_0(0)$	77	−3.0 (6)	−1.2 −2.18 [24]	
$R_0(0)$	195	−3.4 (24)	−1.5	−0.67
$R_0(2)$	195	−1.8 (7)	−0.31	-1×10^{-3}
$R_1(0)$	77	11.8 [16]	5.33 9.8 [24]	
	HD-Ar			
$R_0(1)$	195	−1.6 (2)	−0.21	−0.04
$R_0(2)$	195	4.06 (30)	1.3	-1.7×10^{-3}

These examples have been elaborated to show that collisional propagation or, in other words, details of events during the collision process are important even when the impact approximation is employed. They affect the line-broadening coefficient and are important in the interference effect, particularly to the line asymmetry. It is interesting to note that the interference parameter *a* usually decreases in magnitude when inelastic collisions are included in the calculation. These collisions reduce the degree of indistinguishability between the two transition paths and the interference is accordingly reduced. On the other hand the profile asymmetry usually increases when inelastic collisions are considered. Such results suggest that the collisional interference phenomenon consists of two distinct effects which may be complementary sources of information on intermolecular interactions.

4. COLLISION-INDUCED SPECTRA

Now let us turn to the other common approximation, the quasi-static, and investigate another manifestation of events occurring during collision effects. Here the influence of inelastic collisions on the purely collision-induced spectrum is analyzed through a different approach to the problem of the non-diagonal matrix elements of the propagation.

The sharp rotational lines in the HD spectrum which we have been discussing sit in the observed spectrum on a broad collision-induced background (Fig. 2). In the spectrum of H_2, there are no allowed lines, only a collision-induced component. In Eq. (9) the last term describes the single collision contribution to the collision-induced spectrum. Recall that it depends solely on propagation during the collision. The line shape operator $L(\omega)$ does not appear and the width of the spectral feature is controlled by the duration of the collision.

There has been much activity, and success, in accounting for the observed broad spectral profile of induced transitions based on isotropic intermolecular potentials and *ab initio* calculated induced dipole moment functions.[6] More recently there has been investigation of the role of the anisotropic part of the potential in the formation of the spectral profile.[25,26] To discuss this activity, it is appropriate to work in essentially the opposite to the impact limit, namely the quasi-static approximation (Eq. (8)).

From the last term in (9), the history of a purely induced transition in the system can be specified. The radiator propagates from some initial state at $t = -\infty$ to the moment at the beginning of the collisional event during which the induced dipole operator acts twice, eventually leaving the radiator Omit (Fig. 4) in the final state. The J and m mixing is possible both before the collision occurs as well as during the collision between the instants when the dipole-field interactions take place. It is assumed that the most important contribution to the rotational level mixing comes in a relatively short period of time τ between the instants when the dipole operator acts (when radiator and perturber are more likely to be strongly interacting). It is the part of the time evolution that accounts for the far wing properties of the spectrum.

The Fourier and Laplace transforms of this expression can be calculated for the high frequency region of the spectrum through the stationary phase method[4], which applies to high frequency detuning. (Then τ_C may be short and Eq. (8) can still apply). The matrix elements of the U_e^I operator need to be calculated; since it is an exponential operator, this is a non-trivial task if nondiagonal terms of the form « $J_i m_i J_j m_j \,|U_e^I|\, J_n m_n J_k m_k$ » are to be considered. The problem is resolved by transformation of the wavefunctions to the basis where the V_e^{aI} operator, which describes the anisotropic molecular interactions, is diagonal, specifically through a transformation of the form $\left|\xi\right\rangle = \sum_{Jm} Z_\xi^{Jm} \left| Jm \right\rangle$. With this approach, after integration over velocity and impact parameter, the analytic expression for the absorption coefficient becomes:

$$\alpha(\omega) = \frac{\pi^2}{3} A \sum_{\{Jm\}} \sum_{\xi\phi} \left(Z_\xi^{J_c m_c}\right)^* Z_\xi^{J_g m_g} Z_\phi^{J_i m_i} \left(Z_\phi^{J_a m_a}\right)^* \sum_{\pm\lambda} R(\lambda_\pm) R(\lambda'_\pm)$$

$$\times \frac{\pi}{2} \frac{\left\langle J_g m_g \left| \mu_{1q}(\lambda_\pm) \right| J_\alpha m_\alpha \right\rangle \left\langle J_i m_i \left| \mu_{1q}^{\downarrow}(\lambda'_\pm) \right| J_c m_c \right\rangle}{\left(\left| \frac{\partial V_{\xi\phi}(\lambda_\pm)}{\partial R} \right| \left| \frac{\partial V_{\xi\phi}(\lambda_\pm)}{\partial R} \right| \right)^{1/2}}$$

$$\times \exp\left(- \frac{\left\langle \varphi \middle| \hat{V} \middle| \phi \right\rangle}{kT} \right) \sum_\alpha^B \qquad \text{... (12)}$$

where

$$V_{\xi\phi} = \left\langle \xi \middle| \hat{V}^{aI} \middle| \xi \right\rangle - \left\langle \phi \middle| \hat{V}^{aI} \middle| \phi \right\rangle \qquad \text{... (13)}$$

Here the $\lambda_\pm$ correspond to points of stationary phase; λ_- stands for the point of entering and λ_+ for the point of departing the collision volume; $R(\lambda)$ is the value of the intermolecular separation R at the stationary phase point; A is a constant and $\sum_\alpha^B$ is The Boltzmann factor for state $J_\alpha m_\alpha$.

To understand the implications of this expression it has been applied to a particular case of a simple model. The anisotropic potential is taken to be completely repulsive with an R^{-12} dependence on separation. The induced dipole moment has an exponential R-dependence and the angular symmetry of a quadrupole-induced component. (This model is reminiscent of the early exp-4 model of Van Kranendonk for the induced dipole[5]). These specifications roughly model the H_2-Ar system at high temperature. Potential and dipole moment parameters appropriate to that system were chosen for the calculation.

For H_2-Ar the pronounced lines in the pure rotational induced spectrum involve initial levels with J not exceeding $J_{\max} = 5$. The transitions occur for $\Delta J = 0$ and $+2$. Therefore, lines with initial levels $J = 0, 2, 4$ and $J = +1, 3, 5$ were included in the calculation. These two cases, even and odd J, were treated separately throughout the diagonalization since within the model the even and odd manifolds do not mix with each other. The influence of the nondiagonal matrix elements of the U_e^I operator (which are responsible for the mixing and propagation effects) may be appreciated by concentration on one line and adding corrections by the switching on of various coupling contributions.

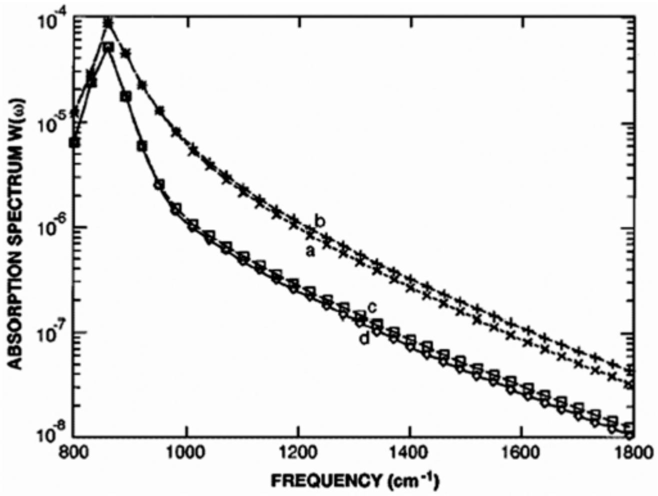

Fig. 4: The calculated absorption spectrum in the region of the S (2) line at 295 K. The distinctions among the curves a, b, c, and d is explained in the text. (Reprinted with permission from W. Glaz and G.C. Tabisz, Phys. Rev. A 54, 3903 (1996). Copyright 1996, The American Physical Society)

Consider the S (2) line, i.e. the transition from $J = 2$ to $J = 4$. As a first step let us deal only with the diagonal elements of the evolution operator, namely «2, 4$|U^I_e|$2, 4» (profile a in Fig. 4). Next allowance is made for the J to vary in the assumed range (0 to 4), i.e. S (0) and S (4) are considered as well, but the diagonal character of the elements «$J_a J_b | U^I_e | J_a J_b$» is maintained. There is still no propagation but influence of lines other than S (2) appears (profile b). The S (2) profile is more intense as the effect from the other lines is purely additive. Then the nondiagonal elements of U^I_e are included and a dramatic change occurs (profiles c and d). The intensity of the S (2) line alone is smaller than when propagation was not taken into account (profile c). When the S (0) and S (4) lines are also allowed to contribute, these contributions tend to lower intensity even more (profile d). Profile c is a single S (2) line but with inelastic collisions or propagation possible between the rotational states, possible between the times at which the dipole operator acts. If there were no line mixing effects, the adding of S (0) and S (4) to S (2) should result in an increase in intensity as between profiles a and b. Instead the intensities are smaller. This result suggests that line mixing and propagation reduce intensity by overcoming the increase due to adding contributions from several lines.

The effect is most important at high frequencies and the gap between *c* and *d* increases with increasing frequency. Direct comparison with experiments is not possible, as not all contributions to the spectrum are included in the model. Notably those from isotropic components of the induced dipole can not be treated by the stationary phase method since, in that case, the potential energy differences that remain are zero.

SUMMARY

How collisional propagation and mixing effects can influence spectral lines shapes have been illustrated. Most of the calculations discussed have been performed for matrix elements involving collision-induced transitions — the case where what occurs during the collision is fact everything, the radiation event included. However it is not only in the far spectral wing where the quasi-static approximation applies that these effects are important. They can influence allowed spectra in the line core, i.e. in the impact approximation regime, both directly and, indirectly, through interference phenomena.

ACKNOWLEDGEMENTS

The author wishes to thank the Natural Sciences and Engineering Research Council of Canada for financial support. This review summarizes work performed with many colleagues and students. He wishes to acknowledge the decisive contributions of P.G. Drakopoulos, J. Cooper, B. Gao, W. Glaz, Z. Lu, B. McQuarrie, J. Nelson, M. Trippenbach, and L. Ulivi. He wishes to thank R. Cameron for her comments on the manuscript.

REFERENCES

[1] H.R. Griem, “Plasma Spectroscopy”, (McGraw-Hill, New York, 1964); A.P. Thorne, “Spectrophysics”, (Chapman and Hall, London, 1988).

[2] C. Boulet, D. Robert, and L. Galatry, “J. Chem. Phys.”, **72**, 751 (1980).

[3] Ph. Marteau, C. Boulet, and D. Robert, “J. Chem. Phys.”, **80**, 3632, (1984).

[4] N. Allard and J. Kielkopf, “Rev. Mod. Phys.”, **54**, 1103, (1982).

[5] H. Welsh, “MTP International Review of Science, Physical Chemistry, Series One, 3, Spectrocopy”, edited by A.D. Buckingham and D. A. Ramsay, (Butterworths, London, 1072), pp. 33.

[6] L. Frommhold, “Collision-Induced Absorption in Gases”, (Cambridge University Press, Cambridge, New York, 1993).

[7] G.C. Wick, “Atti R. Accad. Naz. Lincei”, **21**, 708, (1935).

[8] A. De Lange, E. Reinhold, and W. Ubachs, **21**, 257, (2002).

[9] B. Gao, G.C. Tabisz, M. Trippenbach, and J. Cooper, “Phys. Rev. A”, **44**, 7379, (1991).

[10] A.R.W. McKellar, “Can. J. Phys.”, **51**, 389, (1973).

[11] J.D. Poll, R.H. Tipping, R.D.G. Prasad, and S.P. Reddy, “Phys. Rev. Lett.”, **36**, 248, (1976).

[12] R.H. Tipping, J.D. Poll, and A.R.W. McKellar, “Can. J. Phys.”, **56**, 75, (1978).

[13] R. Herman, R.H. Tipping, and J.D. Poll, “Phys. Rev. A”, **20**, 2006, (1979).

[14] F. Schuller, “The Liouville Space Formalism in Atomic Spectroscopy”, (Heron Press, Sofia, 2002); A. Ben-Reuven, “Adv. Chem. Phys.”, **33**, 235, (1975); U. Fano, “Phys. Rev.”, **131**, 259, (1963).

[15] J.B. Nelson and G.C. Tabisz, “Phys. Rev. Lett.”, **48**, 1393, (1982); (E), **48**, 1870, (1982).

[16] N. Rich and A.R.W. McKellar, “Can. J. Phys.”, **66**, 1648 (1983); A.R.W. McKellar and N. Rich, “Can. J. Phys.”, **62**, 1665, (1984).

[17] P.G. Drakpoulos and G.C. Tabisz, “Phys. Rev. A”, **36**, 5556, (1987); “Phys. Rev.”, **A 36**, 5566, (1987).

[18] L. Ulivi, Z. Lu, and G.C. Tabisz, “Phys. Rev. A”, **40**, 642 (1989).

[19] Z. Lu, G.C. Tabisz, and L. Ulivi, “Phys. Rev. A”, **47**, 1159, (1993).

[20] B. Gao, G.C. Tabisz, and J. Cooper, “Phys. Rev. A”, **46**, 5781, (1991).

[21] B. McQuarrie, G.C. Tabisz, B. Gao and “J. Cooper, Phys. Rev. A” **52**, 1976, (1995).

[22] B. McQuarrie and G.C. Tabisz, “J. Molec. Liq.”, **70**, **159**, (1996).

[23] B. Mc Quarrie and G.C. Tabisz, in “Spectral Line Shapes”, **9**, edited by M. Zoppi and L. Ulivi, (AIP, Woodbury, 1996), 507.

[24] M. Gustafsson and L. Frommhold, “Phys. Rev. A”, **63**, 052514 (2001).

[25] W. Glaz and G.C. Tabisz, “Phys. Rev. A”, **54**, 3903 (1996).

[26] M. Gustafsson, L. Frommhold, D. Bailly, J.P. Bouanich, and C. Brodbeck, “J. Chem. Phys.”, **119**, 12264, (2003).