ФОРМА СПЕКТРАЛЬНОЙ ЛИНИИ ПРИ НИЗКИХ ДАВЛЕНИЯХ: ВОЗМОЖНОСТИ ОБОБЩЕННОЙ ТЕОРИИ С ПРИМЕНЕНИЕМ МЕТОДА КЛАССИЧЕСКИХ ТРАЕКТОРИЙ

С.В. Иванов [1], Ш.Ш. Набиев [2], Я.Я. Понуровский [3]

1) 142190, Московская обл., г. Троицк, ул. Пионерская, д. 2, Институт проблем лазерных и информационных технологий РАН
serg.ivanov.home@mail.ru

2) 123182, г. Москва, пл. Курчатова, д. 1, Институт молекулярной физики РНЦ "Курчатовский институт"

3) 119991, г. Москва, ул. Вавилова, д. 38, ИОФ РАН

INTRODUCTION

Last decades of high-resolution spectroscopy have revealed inefficiency of molecular line shape characterization by ordinary Voigt function if high accuracy is needed for extracted pressure broadening and shifting coefficients. Particularly, it is the case of collisional line narrowing at low pressures (typically 1-760 Torr) usually attributed to Dicke effect and speed dependence of line broadening and shift.

Recent classification [R.Ciurylo 1998] numbers 16 (!!!) different profiles accounting for (or not) several physical mechanisms influencing the shape of isolated spectral line in the impact approximation.

Though numerous, these accountings are not self-consistent. For example, traditional profiles (Galatry, Rautian, speed-dependent Voigt, etc.) widely used in experimental fitting practice contain parameters that serve as only "*ad hoc*" values corresponding to the considered borderline profiles, without referring to the narrowing process actually involved.

◆ **The solution of the inverse spectroscopic problem (i.e. extracting of broadening and shifting coefficients from the line shape) is highly sensitive to measurement errors and to the defects of spectral shape model**

◆ In order to accomplish an accurate and physically substantiated fitting of measured spectra it is necessary to apply self-consistent theory of line profile useable in any condition. It is clear that an adequate theory should include both effects of narrowing (confinement phenomenon and speed dependence of relaxation parameters), naturally being valid for an arbitrary mass ratio of active and buffer molecules. Also such analysis must reflect the correlation which obviously exists between velocity change and dephasing (broadening and shift) in collisions. All indicated demands are fulfilled in recent generalized theory

[R. Ciurylo, A.S. Pine and J. Szudy 2001].

Indicated generalized theory involves several parameters and functions of velocity which should be determined only from special molecular scattering calculations (namely, parameters of "hardness" of collisions, of correlation of velocity-changing and dephasing collisions, diffusion constant, speed dependence of line broadening and shift).

To avoid importing systematic errors, scattering calculations of all above mentioned parameters and functions should employ:

- realistic anisotropic intermolecular potential energy surface (PES)
- accurate simulation of molecular motion during collision

- **Classical trajectory method is very promising to this effect being quite accurate, rapid and allowing for visual and self-consistent characterization of internal (rotational , vibrational) and translational motions of colliding molecules**

Generalized theory of line profile [Ciurylo et al. 2001] includes:

- speed-dependence of broadening and shift
- partial "hardness" of collisions
- partial correlation of velocity-change and broadening in collisions

Spectral distribution of line intensity

$$I(\omega) = Re\left\{\frac{G(\omega)}{1-\pi H(\omega)}\right\}$$

$$G(\omega) = \frac{1}{\pi}\int_0^\infty dt \int d^3\vec{v} \int d^3\vec{r} \cdot W_{\zeta(v)}(\vec{r},t;\vec{v}) \cdot W_M(\vec{v})$$

$$\times \exp\{-\xi(v) - i\chi(v) - \beta(v)t - \Gamma(v)t + i[\omega - \omega_0 - \Delta(v)]t - i\vec{k}\vec{r}\}$$

$$H(\omega) = \frac{1}{\pi}\int_0^\infty dt \int d^3\vec{v} \int d^3\vec{r} \cdot W_{\zeta(v)}(\vec{r},t;\vec{v}) \cdot W_M(\vec{v})$$

$$\times \beta(v)\exp\{-\beta(v)t - \Gamma(v)t + i[\omega - \omega_0 - \Delta(v)]t - i\vec{k}\vec{r}\}$$

Maxwellian distribution at gas temperature T

$$W_M(\vec{v}) = \left(\frac{m_A}{2\pi k_B T}\right)^{3/2} exp\left(-\frac{m_A v^2}{2k_B T}\right)$$

Chandrasekhar distribution (probability of finding a particle at the time **t** at the position **r**, if the initial position and velocity were 0 and **v**)

$$W_{\zeta(v)}(\vec{r},t;\vec{v}) = \left(\frac{A(v)}{\pi}\right)^{3/2} \exp\left(-A(v)[\vec{r} - \vec{v}\left(1-e^{-\zeta(v)t}\right)/\zeta(v)]^2\right)$$

$$A(v) = \frac{m_A \zeta^2(v)/(2k_B T)}{2\zeta(v)\cdot t - 3 + 4e^{-\zeta(v)t} - e^{-2\zeta(v)t}}$$

Generalized theory of line profile *(continued)*

ω - frequency, ω_0 – line center, $\mathbf{k = \omega/c}$ - wave number,
$\mathbf{m_A}$ – mass of active molecule, **v** - absolute speed of active molecule

The Dicke narrowing and the correlation between dephasing and velocity-changing collisions are described by two speed-dependent parameters $\zeta(v)$ and $\beta(v)$

- Effective frequency of "soft" collisions $\zeta(\mathrm{v}) = (1-\varepsilon)\{\nu_{\mathrm{diff}} - \eta[\Gamma(\mathrm{v}) + \mathrm{i}\Delta(\mathrm{v})]\}$
- Effective frequency of "hard" collisions $\beta(\mathrm{v}) = \varepsilon\{\nu_{\mathrm{diff}} - \eta[\Gamma(\mathrm{v}) + \mathrm{i}\Delta(\mathrm{v})]\}$
- "Diffusion" frequency of collisions (D is diffusion coefficient) $\nu_{\mathrm{diff}} = \dfrac{k_B T}{m_A D}$
- Parameter ε - describes the "hardness" of the velocity-changing collisions (ε = 0 – pure soft , ε =1 – pure hard collision)
- Parameter η - describes partial correlation between velocity-changing and dephasing collisions (η = 0 – no correlation , η = 1 – full correlation)

<u>Functions of absolute speed **v**:</u>
Γ**(v)** – line-width (HWHM), Δ**(v)** – line-shift ,
χ**(v)** , ξ**(v)** – additional functions
(arising either from finite duration of collisions (non-impact) or line-mixing)

- Here we set ξ (v) +i χ (v) =0

- <u>Limitations of theory:</u>

$\eta_{\mathrm{width}} = \eta_{\mathrm{shift}}$
ν_{diff} – no **v** - dependence

Particular cases of generalized line profile

(no dispersion asymmetry: $\xi(v) + i\chi(v) = 0$)

Speed-dependent effects included: $\Gamma = \Gamma(v)$, $\Delta = \Delta(v)$

$\eta=0$ Speed-dependent asymmetric Rautian-Sobel'man profile (Ciurylo 1998)
$\varepsilon=1$ Partially correlated speed-dependent Rautian profile (hard collisions, Pine 1999)
$\eta=0$ Rautian-Sobel'man profile (soft&hard collisions, Rautian&Sobel'man 1967)
$\varepsilon=1$, $\eta=0$ Speed-dependent Nelkin-Ghatak profile (hard collisions, Nelkin-Ghatak 1964)
$\varepsilon=0$, $\eta=0$ Speed-dependent Galatry profile (soft collisions, Rautian&Sobel'man 1967)
$\eta = 0$, $\nu_{diff} = 0$ (no velocity-changing collisions) Speed-dependent Voigt profile (Berman 1972, Ward-Coopper-Smith 1974)
$\zeta(v) = (1-\varepsilon)\nu_{diff}$, $\beta(v) = \varepsilon\nu_{diff} - [\Gamma(v) + i\Delta(v)]$ - fully correlated speed-dependent Rautian-Sobel'man profile (Lance&Robert 1998)

No speed-dependent effects: $\Gamma(v)=const$, $\Delta(v)=const$

$\varepsilon=0$, $\eta=1$ Correlated Galatry profile (soft collisions, Rautian&Sobel'man 1967)
$\varepsilon=0$, $\eta=0$ Galatry profile (soft collisions, Galatry 1961)
$\varepsilon=1$, $\eta=0$ Nelkin-Ghatak profile (hard collisions, Nelkin-Ghatak 1964)
$\eta=0$ Rautian-Sobel'man profile (soft&hard collisions, Rautian&Sobel'man 1967)
$\eta = 0$ $\nu_{diff} = 0$ (no velocity-changing collisions) Voigt profile

Required information for operation with generalized speed-dependent line profile :

1) dependence of line width Γ**(v)** and line shift Δ**(v)** on absolute velocity **v** of active molecules;

2) correlation coefficients between velocity changing processes and broadening (η_w) and shifting (η_s) of given spectral line in collisions;

3) "diffusion" frequency of collisions ν_{diff} ;

4) parameter ε of "hardness" of collisions

Bulk of this information was produced by detailed classical trajectory calculation of HF-Ar collisions:

- Exact 3D classical trajectory scheme [M.D.Pattengill 1977]
- *Ab initio* vibrationally dependent HF-Ar PES H6 (4,3,2) [J.Hutson 1992]
- Classilcal theory for impact broadening and shift [R.Gordon 1966]
- Computational scheme [S.Ivanov et al. 2005; S.Ivanov, O.Buzykin 2008]

Speed-dependence of line width Γ(v) and shift Δ(v) on absolute velocity v of active molecule

$$\Gamma(\mathrm{v}) = \int_0^\infty \mathrm{f}(\mathrm{v}_{\mathrm{rel}} \,|\, \mathrm{v})\,\Gamma(\mathrm{v}_{\mathrm{rel}})\,d\mathrm{v}_{\mathrm{rel}}, \quad \Delta(\mathrm{v}) = \int_0^\infty \mathrm{f}(\mathrm{v}_{\mathrm{rel}} \,|\, \mathrm{v})\,\Delta(\mathrm{v}_{\mathrm{rel}})\,d\mathrm{v}_{\mathrm{rel}}$$

$$\mathrm{f}(\mathrm{v}_{\mathrm{rel}} \,|\, \mathrm{v}) = \frac{4\mathrm{v}_{\mathrm{rel}}}{\pi \mathrm{v} \bar{\mathrm{v}}_2}\, sinh\left(\frac{8\mathrm{v}\mathrm{v}_{\mathrm{rel}}}{\pi \bar{\mathrm{v}}_2^2}\right) exp\left(-\frac{4(\mathrm{v}^2 + \mathrm{v}_{\mathrm{rel}}^2)}{\pi \bar{\mathrm{v}}_2^2}\right)$$

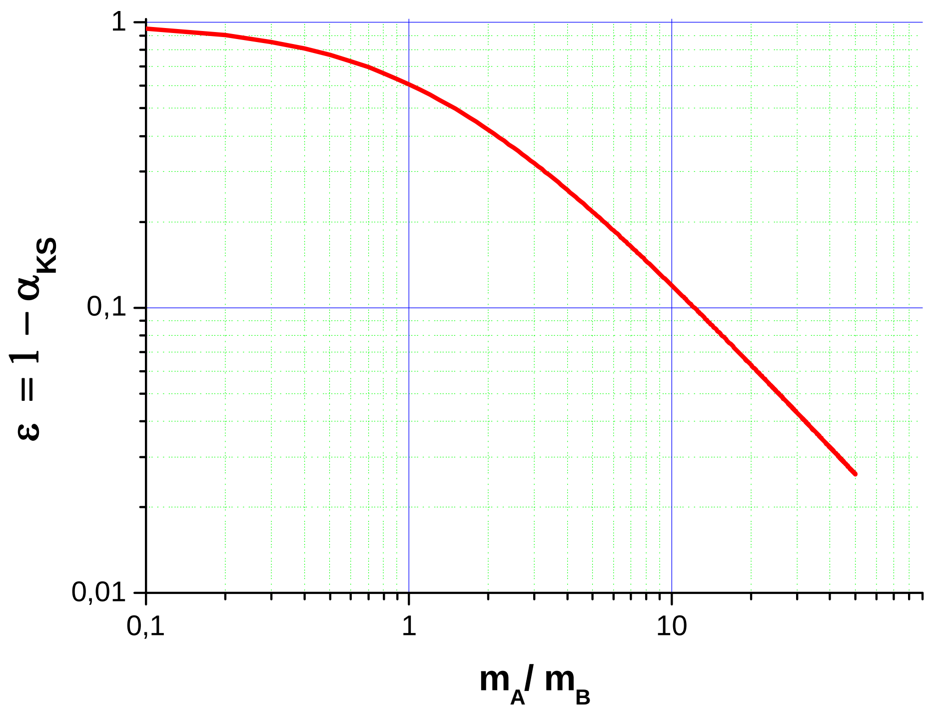
$f(v_{rel}|v)$ is conditional Maxwell distribution [Luijendijk 1977, Pickett 1980];
v_{rel} is relative speed of colliding pair, v is absolute speed of active molecule
v_2 is rms speed of the perturber molecule (Ar)

Keilson-Störer model for ε evaluation

$$\varepsilon = 1-\alpha_{KS} = 1-m_A/(m_A+m_B)+\frac{1}{2}\left[m_B/(m_A+m_B)\right]\times$$

$$\times\left[\theta^{-3}(1-2\theta^2)\mathrm{erf}(\theta)-\theta^{-2}\mathrm{erf}(-\theta^2)\right]\cdot\left[\mathrm{erf}(-\theta^2)+(2\theta+\theta^{-1})\mathrm{erf}(-\theta^2)\right]^{-1}$$

$$\theta=(m_B/m_A)^{1/2}, \quad \mathrm{erf}(\theta)=\int_0^\theta exp(-y^2)dy$$



m_A , m_B are masses of active and buffer molecules

HF-Ar	ε = 0,77
C_2H_2-Ar	ε = 0,71
C_2H_2-He	ε = 0,17

Parameter η - partial correlation between velocity-changing and dephasing collisions

It is simply the correlation coefficient of two random processes X and Y (X = x_i - change of relative velocity and Y = yi – line-broadening (or shift) in collisions i = 1,.., N)

$$\eta = r_{XY} = \frac{C_{XY}}{\sigma_X \sigma_Y}, \quad C_{XY} \approx (N >> 1) \approx \frac{1}{N}\sum_{i=1}^{N} x_i y_i - \bar{x}\cdot\bar{y},$$

$$\sigma_X^2 = \frac{1}{N}\sum_{i=1}^{N}(x_i - \bar{x})^2, \quad \sigma_Y^2 = \frac{1}{N}\sum_{i=1}^{N}(y_i - \bar{y})^2, \quad -1 \le r_{XY} \le +1$$

◆ "Diffusion" frequency of collisions

χ - deflection angle of rel. velocity in the collision

n_B – buffer molecules number density

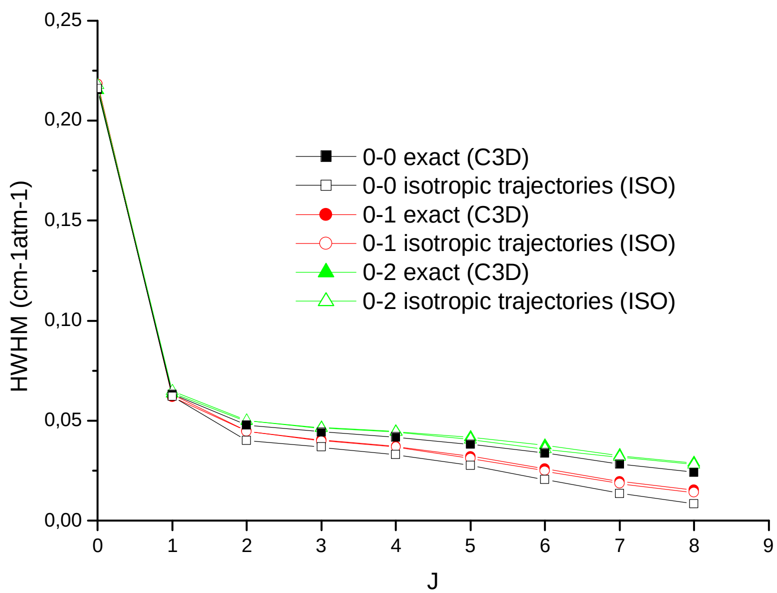
b – impact parameter

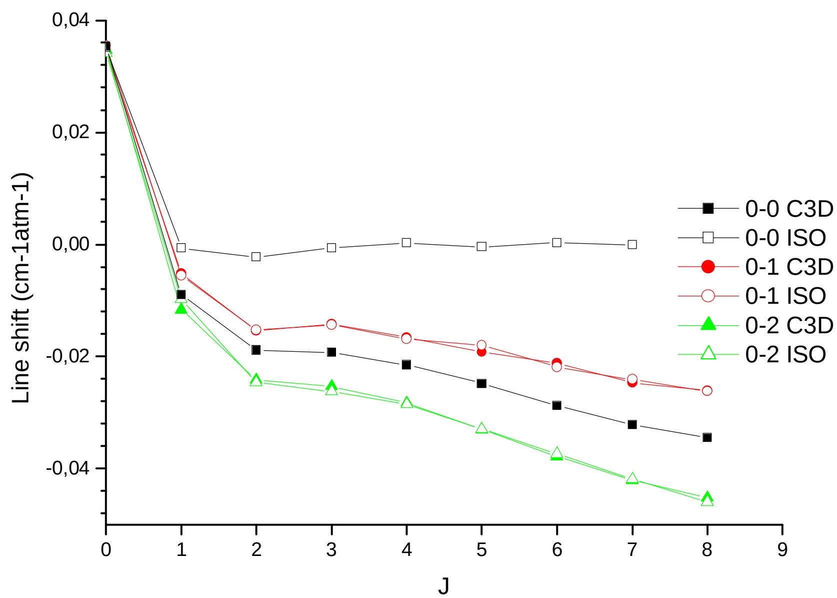
O – initial orientations

$$\nu_{diff} = \frac{4\pi}{3}\frac{\mu}{m_A}\frac{n_B}{v_P^2}\left\langle v_{rel}^2(1-\cos\chi)\right\rangle_{b, v_{rel}, \vec{O}}$$

$$\mu = \frac{m_A}{m_A + m_B}, \quad v_P = \sqrt{\frac{2k_BT}{\mu}}$$

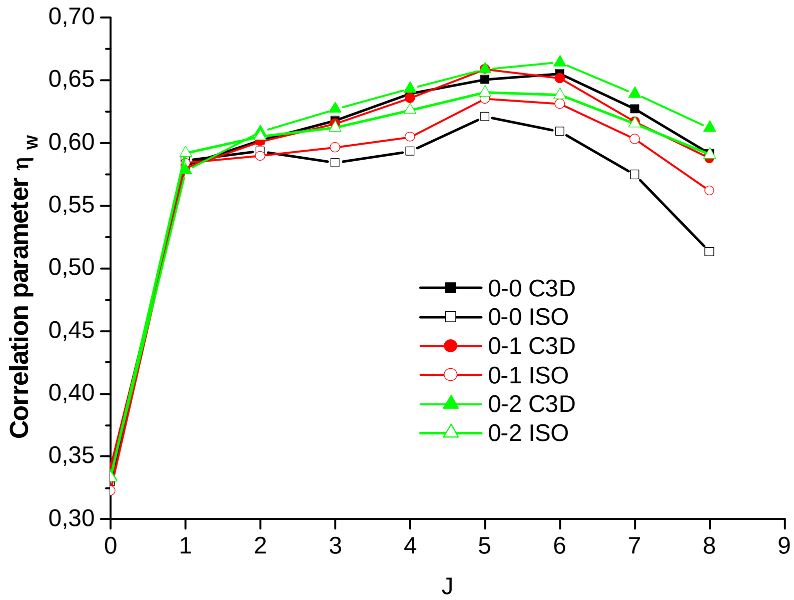
Widths and shifts of HF lines in R-branch of 0-v absorption band. HF-Ar at T=296 K

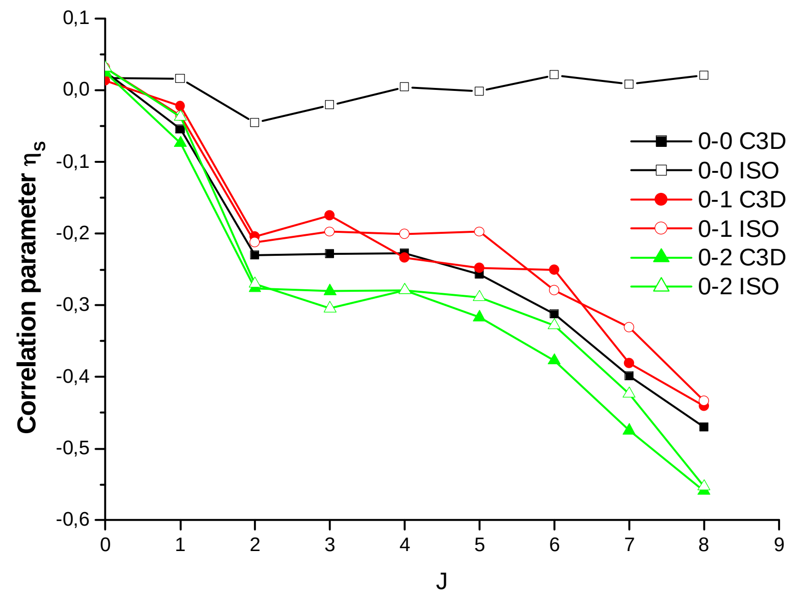




- Classical ISO trajectories are reasonable in width and shift calculations except of 0-0 band

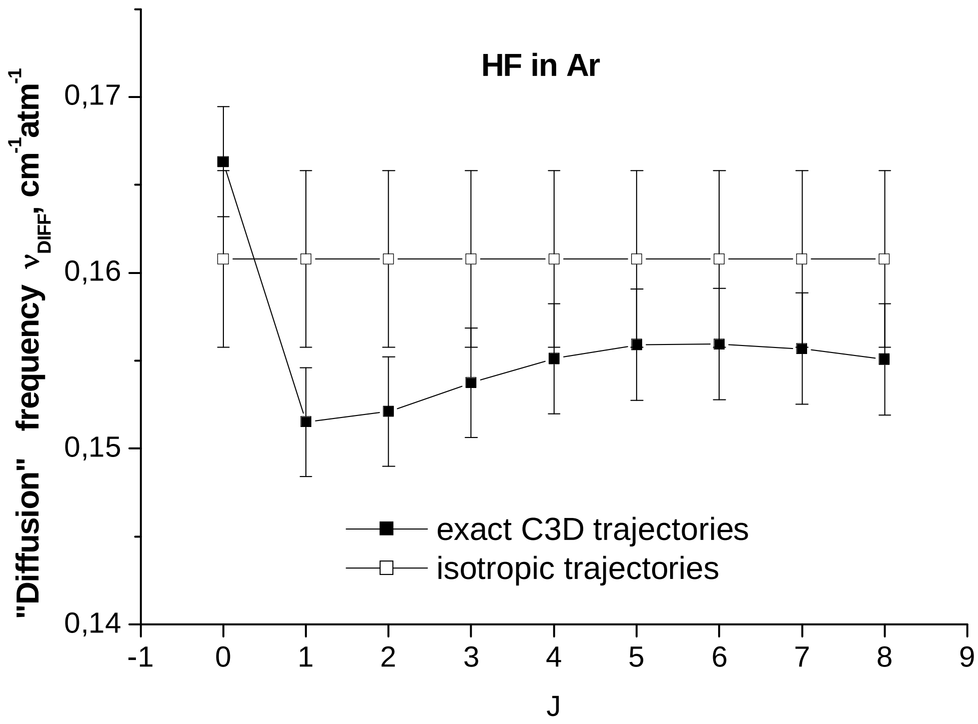
Correlation parameters η_w , η_s for dephasing and velocity changing processes in collisions. HF-Ar T=296 K





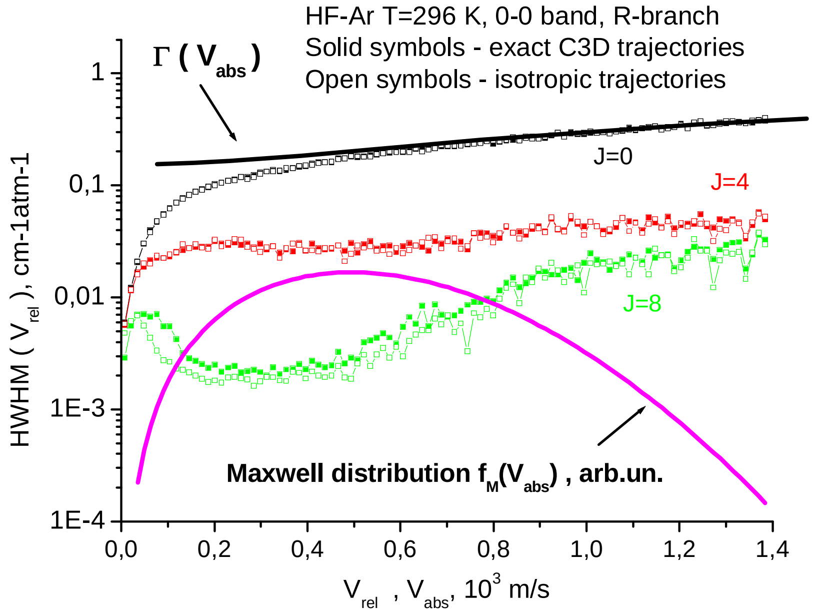
- C3D and ISO calculations accord reasonably (except of 0-0 band)
- Correlation parameter η_s absolutely does not coincide with η_w. This may lead to additional errors. This is principal defect of general line shape theory of Ciurylo, Pine and Szudy
- Vibrational dephasing plays remarkable role in line-shifting

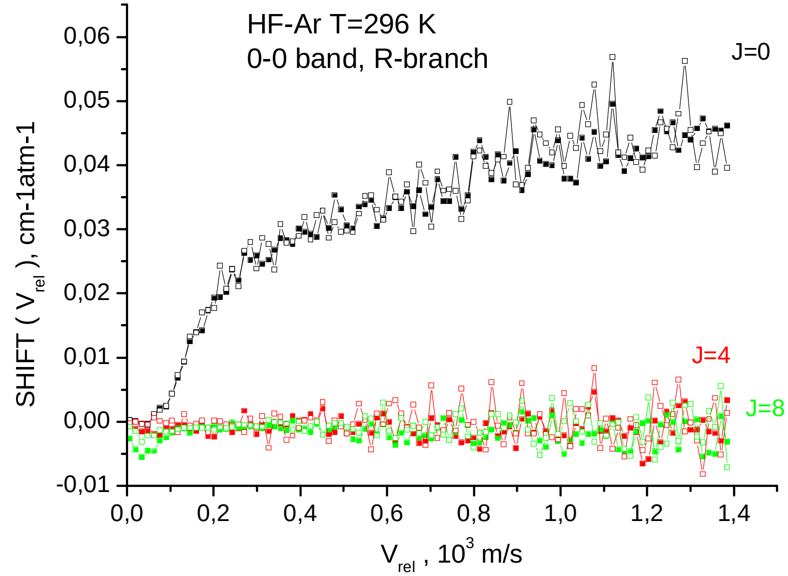
"Diffusion" frequency ν_{diff} of HF molecules in mixture with Ar at T=296 K



- Systematic error imported by isotropic trajectories reaches 6%

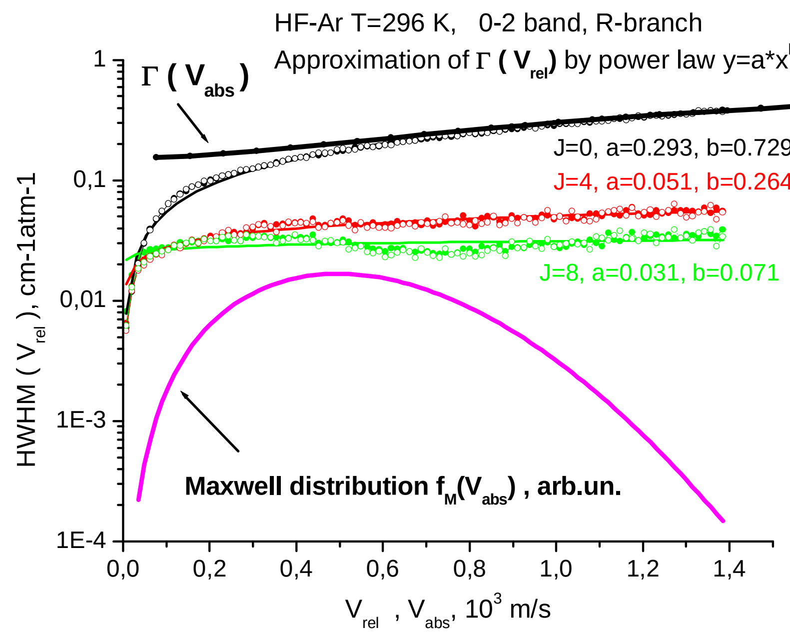
Velocity dependencies of HF line width and shift





◆ ISO trajectories work reasonably in predicting velocity dependence of line width Γ(v) and shift Δ(v) . But not accurately.

◆ Power law y=a·xb is not always an adequate approximation for Γ(v)



CONCLUSIONS

- Classical trajectory method is an efficient tool for obtaining all necessary information for application of general speed-dependent line shape theory in fitting practice .
- Correlation parameter η_S for line shift absolutely does not coincide with that for line width η_W . This is one of possible defects of general line shape theory of Ciurylo, Pine and Szudy.
- Systematic errors for HF diffusion frequency in Ar mixture imported by the application of isotropic trajectories reach 6%.
- Isotropic trajectories generally work reasonably in predicting velocity dependencies of line width $\Gamma(v)$ and line shift $\Delta(v)$ for HF lines in Ar mixture. But not always accurately.
- Power law $y=a \cdot x^b$ is not always an adequate approximation for speed dependence of line width $\Gamma(v)$.

ACKNOWLEDGMENTS

Authors are grateful to Oleg Buzykin for the assistance in trajectory computations. Francois Rohart is acknowledged for sending his articles helping to look into the problem. The authors thank Jeremy M. Hutson for providing us with H6 (4,3,2) potential in the form of FORTRAN code.

References

R. Ciurylo. Shape of pressure and Doppler- broadened spectral lines in the core and near wings// *Phys. Rev. A, V.*58, P. 1029-1039 (1998).

R. Ciurylo, A.S. Pine, J. Szudy. A generalized speed-dependent line profile combining soft and hard partially correlated Dicke-narrowing collisions// *JQSRT,* V.68, P. 257-271 (2001).

J. M. Hutson. Vibrational dependence of the anisotropic intermolecular potential of Ar-HF// *J. Chem. Phys.*, V. 96, No. 9, P. 6752- 6767 (1992).

S. Green, J. Hutson. Spectral line shape parameters for HF in a bath of Ar accurately predicted by a potential inferred from the spectra of the van der Waals dimer// *J. Chem. Phys.*, V.100, P. 891-898 (1994).

J.-M. Hartmann, C. Boulet. Line shape parameters for HF in a bath of Ar as a test of classical path model// *J. Chem. Phys.*, V. 113, No. 20, P. 9000-9010 (2000).

H.M. Pickett. Effects of velocity averaging on the shapes of absorption lines// *J. Chem. Phys.*, V.73, No. 12, P. 6090-6094 (1980).

S.C.M. Luijendijk. On the shape of pressure-broadened absorption lines in the microwave region// *J. Phys. B: Atom. Molec. Phys.*, V. 10, No. 9, P. 1735-1739 (1977).

J. Keilson, J.E. Störer. On Brownian motion, Boltzmann's equation and the Fokker-Planck equation// Quart. Appl. Math., V.10, P. 243-253 (1952).

M. Borenstein, W.E. Lamb. Effect of velocity changing collisionjs on the output of a gas laser// *Phys. Rev. A, V.*5, N 3, P. 1029-1039 (1972).

B. Lance, D. Robert. An analytical model for collisional effects on spectral line shape from the Doppler to collisional regime// *J. Chem. Phys.*, V. 109, P. 8283-8288 (1998).

References (continued)

A.S. Pine. Asymmetries and correlations in speed-dependent Dicke-narrowed line shapes of argon-broadened HF// *JQSRT*, V. 62, P. 397-432 (1999).

S.G. Rautian, I.I. Sobel'man. The effect of collisions on the Doppler broadening of spectral lines// *Sov. Phys. Uspekhi*, V. 9, P. 701-716 (1967).

L. Galatry. Simultaneous effect of Doppler and foreign gas broadening on spectral lines// *Phys. Rev., V.* 122, P. 1218-1223 (1961).

R.H. Dicke. The effect of collisions upon the Doppler width of spectral lines// *Phys. Rev., V. 89*, P. 472-473 (1953).

M. Nelkin, A. Ghatak. Simple binary collision model for Van Hove's $G_s(r,t)$ // *Phys. Rev., V. 135*, P. A4-A9 (1964).

P.R. Berman. Speed-dependent collisional width and shift parameters in spectral profiles // *JQSRT*, V. 12, P. 1331-1342 (1972).

J. Ward, J. Cooper, E.W. Smith. Correlation effects in the theory of combined Doppler and pressure broadening – I. Classical theory// *JQSRT*, V. 14, P. 555-590 (1974).

R.G. Gordon. Theory of the width and shift of molecular spectral lines in gases// *J. Chem. Phys.*, V. 44, No. 8, 3083-3089 (1966).

M.D. Pattengill. On the use of body-fixed coordinates in classical scattering calculations: planar trajectory approximation for rotational excitation// *J. Chem. Phys*., V. 66, No. 11, 5042-5045 (1977).

S.V. Ivanov, L. Nguyen, J. Buldyreva. Comparative analysis of purely classical and semiclassical approaches to collision line broadening of polyatomic molecules : I. C2H2-Ar case // J. Molec. Spectrosc., 2005, V. 233, P. 60-67.

S.V. Ivanov, O.G. Buzykin. Classical calculation of self-broadening in N2 Raman spectra//Mol. Phys., 2008, V. 106, No. 9-10, P. 1291-1302.