ON THE PRESSURE BROADENING OF THE MOLECULAR SPECTRA II. THE MOLECULAR LINE SHAPE IN THE DOPPLER LIMIT*

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The molecular spectrum line shape within the Doppler limit has been investigated. The resultant line shape appears to be velocity dependent Voigt profile. The semiclassical expression for the line shape has been derived on the assumption that the potential is composed of a core potential and a multipole term. The resultant formula holds true for interactions of order higher than dipole-dipole.

1. Introduction

The statistical correlation between the Doppler and pressure mechanisms of line shape broadening has been the subject of numerous papers [1–11]. A consideration of molecular lines in this particular theory based on the Liouville space formalism has been presented in the paper [12]. In the impact theory limit the succesive collisions are separated by a large time. However, they are correlated, for the perturber velocity distribution seen by radiator depends on its own velocity and thus on its last collision. The above fact seriously complicates the line shape calculation even if the semiclassical description is used. Particularly in rotational molecular spectra both m-degenerate radiative states $|i\rangle$, $|f\rangle$ are strongly perturbed and one must take into account the influence of collision-induced velocity changes of the radiator on both states. The nonspherical potential in this problem involves additional complications, whence the simple model is hard to create.

In this work the theory of molecular spectra line shape for the low pressure region, when Doppler broadening is larger than the collisional one, has been developed. In the second Section some basic assumptions and formulae are presented. The general formula of velocity dependent operator relaxation [12] was used here. Assuming the collision-induced changes of velocity of radiator can be neglected, the velocity dependent Voigt profile of molecular line has been derived.

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In the third Section a semiclassical model is proposed. The formula for the velocity dependent half-width in straight path approximation with the assumption of multipole potential interaction and isotropic effective potential core is derived. The above expressions are true for the multipole interactions of higher ranges than dipole-dipole.

2. The line shape

In paper [12] the impact theory of relaxation collision effects with regard to the correlation between pressure and Doppler line broadening as applied to molecules has been presented.

In the elastic scattering approximation the relaxation operator may be shown to be a combination of on-the-energy-shell T transition matrix and can be split into diagonal and non-diagonal parts in the eigenvalues state $e_{if}(\vec{\kappa}\vec{p}_0 JM)$ of the momentum and the whole angular momentum operators of the radiator. In the trace metric of the Liouville space as defined for the two operators A and B of Hilbert-Schmidt by the scalar product

$$(A, B) = \mathrm{Tr}\,(A^{+}B), \tag{1}$$

the molecular relaxation operator gets the following formula

$$(e_{if}(\vec{\kappa}\vec{p}_0 JM), \vec{\Phi} e_{if}(\vec{\kappa}\vec{p}'_0 J'M')) = \Phi_{if}(\vec{p}_0)\delta(\vec{p}_0 - \vec{p}'_0)\delta_{JJ'MM'} + \Pi_{if}(\vec{p}_0, \vec{p}'_0; JJ'MM'); \tag{2}$$

eigenvectors $e_{if}(\vec{\kappa}\vec{p}_0 JM)$ form the orthonormal basis

$$(e_{if}(\vec{\kappa}\vec{p}_0 JM), e_{if}(\vec{\kappa}\vec{p}'_0 J'M')) = \delta_{JJ'}\delta_{MM'}\delta(\vec{p}_0 - \vec{p}'_0), \tag{3}$$

where $\vec{\kappa}$ is the given difference of the final state momentum and the initial one $\vec{p}_0$ of the radiator and J and M label the quantum numbers of the whole angular momentum operator of the radiator.

The diagonal part of the relaxation operator $\Phi_{if}(\vec{p}_0)$ in the isotropic environment is the following:

$$\Phi_{if}(\vec{p}_0) = n(2\pi)^3 \left\langle \frac{\sum\limits_m \langle j_i m v_i \vec{p}\alpha | T | j_i m v_i \vec{p}\alpha \rangle}{2j_i + 1} + \frac{\sum\limits_m \langle j_f m v_f \vec{p}\alpha | T | j_f m v_f \vec{p}\alpha \rangle^*}{2j_f + 1} \right\rangle_{\mathrm{av}}, \tag{4}$$

where T is the transition matrix, $j_i v_i$ and $j_f v_f$ denote rotational and vibrational quantum numbers respectively of the initial state $|i\rangle$ and the final one $|f\rangle$, m stands for a magnetic number, α is a set of quantum numbers of the internal motion of the perturber, $\vec{p}$ is a relative motion momentum and n indicates the density of the perturber.

Finally by $\langle \ldots \rangle_{\mathrm{av}}$ is meant the average over the perturber states of momentum and internal motion with the canonical ensemble whose eigenvalues of the density matrix are as follows:

$$\varrho(p, \alpha) = \frac{1}{Q} e^{\frac{-\beta p^2}{2m}} \varrho(\alpha), \tag{5}$$

where Q is the statistical sum and β is the inverse product of the Boltzman constant and temperature and $\varrho(\alpha)$ denotes the Boltzman distribution function.

In analogy to the conventional theory of pressure broadening of a line (when the motion of the radiator is not taken into account) $\Phi_{if}(\vec{p}_0)$ can be viewed as the term due to "phase-interrupting" collisions [13].

The nondiagonal part of the relaxation operator is supplied by:

$$\Pi_{if} = in(2\pi)^4(2J+1)(2J'+1)\sum_{\alpha'}\sum_{\substack{m_i m_f \\ m_i' m_f'}}(-1)^{-m_f-m_f'}\begin{pmatrix} j_f & J & j_i \\ -m_f & M & m_i \end{pmatrix}$$

$$\times\begin{pmatrix} j_f & J' & j_i \\ -m_f' & M' & m_i' \end{pmatrix}\langle\langle j_f m_f' v_f \vec{p}'\alpha'|T|j_f m_f v_f \vec{p}\alpha\rangle^*\delta(\varepsilon-\varepsilon')\langle j_i m_i v_i \vec{p}\alpha|T|j_i m_i' v_i \vec{p}'\alpha'\rangle\rangle_{\text{av}}, \quad (6)$$

where (: : :) stands for $3j$ Wigner symbol, ε for the internal motion energy.

It is noticeable that the above non-diagonality proves to be a consequence of the translational-internal coupling scheme of the system, since there is some amount of the angular momentum coupling between translational and internal of degrees freedom. Π_{if} includes the velocity-dependent effect (Dicke narrowing) which has been observed in rotational spectra [14, 15]. In general both the velocity-dependent and "phase interrupting" collisions effect cannot be separated. However, respectively to their different pressure dependence they can be separated if the contributions up to the first order only are retained.

In the so-called Doppler limit i. e. in the case when the Doppler half-width is larger than the collisional half-width it is possible to neglect collision-induced changes in the radiator's velocities [16]. It is equivalent to neglecting for the calculation of the line profile, the input arising from the nondiagonal part of the relaxation operator Π_{if} (see Appendix). If the radiation emitted from the gas is spherically symmetric as has been formerly assumed, then the corresponding line shape of the dipole vibrational-rotational transition results in the velocity-dependent Voigt profile:

$$I(\omega) = \frac{1}{\pi}\int d_3\vec{p}_0\,\varrho(\vec{p}_0)\,\frac{\Gamma_{if}(\vec{p}_0)}{\left(\omega-\omega_{if}-\frac{\vec{\kappa}\vec{p}_0}{m}-\Delta_{if}(\vec{p}_0)\right)^2+(\Gamma_{if}(\vec{p}_0))^2}, \quad (7)$$

where

$$\Gamma_{if}(\vec{p}_0) = \Gamma_i(\vec{p}_0)+\Gamma_f(\vec{p}_0), \quad (8)$$

$$\Delta_{if}(\vec{p}_0) = \Delta_i(\vec{p}_0)+\Delta_f(\vec{p}_0) \quad (9)$$

are collisional speed dependent widths and shifts determined respectively as the imaginary and real part of $\Phi_{if}(\vec{p}_0)$.

The above expression describes the deviations from the standard Voigt profile [7, 17]. This deviation is due mainly to the finite life time of the radiator with the initial momentum $\vec{p}_0$. As compared with (7) the initial formula used in this paper has been fairly simplified.

That is to say, as has been suggested in the theory of gas lasers [18, 19] the velocity dependent relaxation operator $\Phi_{if}(\vec{p}_0)$ may be averaged over the momentum components perpendicular to the z-axis i. e. to the momentum transferred from the electromagnetic field to the radiator. Instead of (4) we get therefore:

$$\Phi_{if}(p_{0z}) = \tfrac{1}{2}\,(\Phi_i(p_{0z}) - \Phi_f^*(p_{0z})), \tag{10}$$

where

$$\Phi_a(p_{0z}) = 2n(2\pi)^3 \int d_3\vec{p}_1 \varrho^{\frac{1}{2}}\left(\frac{p_1^2}{2m_1}\right) \int d_3\vec{p}_1 \varrho^{\frac{1}{2}}\left(\frac{p_1'^2}{2m_1}\right)$$

$$\times \int d_2\vec{p}_{0\perp} \varrho^{\frac{1}{2}}\left(\frac{p_{0\perp}^2}{2m_0}\right) \int d_2\vec{p}'_{0\perp} \varrho^{\frac{1}{2}}\left(\frac{p_{0\perp}'^2}{2m_0}\right) \delta_3(\vec{P}-\vec{P}')\delta(\vec{p}_{0\perp}-\vec{p}'_{0\perp})$$

$$\times \left\langle \frac{\sum\limits_m \langle j_a m v_a \vec{p}\alpha | T | j_a m v_a \vec{p}\alpha\rangle}{2j_a+1} \right\rangle_{\text{av}}, \qquad a = i \text{ or } f. \tag{11}$$

$\vec{P}, \vec{p}_1$ being here the momentum of the center of mass and the momentum of the perturber respecively, m_1, m_0 standing respectively for the mass of the perturber and the mass of the radiator. Next in view of the fact that the diagonal elements of the T matrix are dependent only on the magnitude of the relative momentum p one can give (11) in a simpler form [20].

$$\Phi_a(p_{0z}) = 2n(2\pi)^4 \left(\frac{\beta}{4\pi m_0}\right)^{\frac{3}{2}} \frac{m_1}{\mu^2} \int_0^\infty dp_\perp p_\perp \varrho^{\frac{1}{2}}\left(\frac{p_\perp^2}{2m}\right)$$

$$\times \int_{-\infty}^{\infty} dp_{1z} \varrho^{\frac{1}{2}}\left(\frac{p_{1z}^2}{2m_1}\right) \left\langle \frac{\sum\limits_m \langle j_a m v_a \vec{p}\alpha | T | j_a m v_a \vec{p}\alpha\rangle}{2j_a+1} \right\rangle_{\text{av}}, \tag{12}$$

where μ is the reduced mass and $p_\perp$ and p_{1z} are the perpendicular component of the relative momentum and the z-components of the perturber momentum respectively.

Again, for the sake of simplicity one takes up the rigid rotator model for which the Hamiltonian of the vibrational energy of the radiator and the perturber is treated as a constant of motion. Hence it is necessary to neglect the dependence of the T matix elements on the vibrational states.

In addition we assume here the shifts Δ_{if} are to be small so they can be neglected [21].

Finally, in this approximation for the line shape function of the molecular rotational spectra lines we arrive at

$$I(\omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} dp_{0z} \varrho(p_{0z}) \frac{\Gamma_i(p_{0z}) + \Gamma_f(p_{0z})}{\left(\omega - \omega_{if} - \dfrac{\kappa p_{0z}}{m_0}\right)^2 + (\Gamma_i(p_{0z}) + \Gamma_f(p_{0z}))^2}, \tag{13}$$

where

$$\Gamma_a(p_{0z}) = 2n(2\pi)^4 \operatorname{Im} \left\langle \frac{\sum_m \langle j_a m\vec{p}\alpha|T|j_a m\vec{p}\alpha\rangle}{2j_a+1} \right\rangle_{\perp,\mathrm{av}}, \tag{14}$$

in which $\langle \ldots \rangle_{\perp,\mathrm{av}}$ alongside with (12) shows the average over the perpendicular component of the relative momentum and over the z-component the perturber momentum and over the internal motion of the perturbers.

3. *Semiclassical model*

The exact calculation of the velocity-dependent Voigt profile (13) appears excessively complex. In order to facilitate the problem a semiclassical approach is assumed in which translational motion is regarded classically while their internal motion quantum mechanically. The easiest way is to evaluate the diagonal elements of the T matrix (14) in the eikonal approximation [22]. For this purpose a straight-line trajectory is assumed by the relative velocity and impact parameter. In this approximation the diagonal elements of the T transition operator may be expressed as follows:

$$\langle j_a m\vec{p}\alpha|T|j_a m\vec{p}\alpha\rangle = \frac{ip}{\mu(2\pi)^2} \int_0^\infty bdb\langle j_a m\alpha|S(p,b)-1|j_a m\alpha\rangle, \tag{15}$$

where $S(p, b)$ is the classical path scattering operator for the interaction between the radiator and the perturber.

Now some standard methods of the broadening pressure theory (that is when the Doppler effect is neglected) can be included. We assume that the whole Hamiltonian of the system of two rigid colliding molecules is of the form

$$H = H_0 + V_0(t) + V_1(t), \tag{16}$$

where V_0 is the isotropic potential core, V_1 is anisotropic multipole long-range potential of the shape [23]

$$V_1(t) = \sum_{l_1 l_2} C_l(l_1 l_2) T_{l\mu}(l_1 l_2) \frac{Y_{l\mu}(\Omega)}{r^{l+1}(t)}, \tag{17}$$

where

$$T_{l\mu} = \sum_{\mu_1\mu_2} \begin{pmatrix} l_1 & l_2 & l \\ \mu_1 & \mu_2 & \mu \end{pmatrix} Y_{l_1\mu_1}(\vec{r}_1) Y_{l_2\mu_2}(\vec{r}_2) \tag{18}$$

is a tensor operator of rank l.

The unit vectors $\vec{r}_1$ and $\vec{r}_2$ denote the molecule orientation and Ω is the orientation of $\vec{r}$, $Y_{l\mu}(\Omega)$ are spherical harmonics and $C_l(l_1 l_2)$ is given by

$$C_l(l_1 l_2) = (-1)^{l_1}\left(\frac{4\pi(2l+1)!}{(2l_1+1)!(2l_2+1)!(2l+1)}\right)^{\frac{1}{2}}. \tag{19}$$

Here Q_{ls} = l-th multipole moment of molecule s and $l = l_1+l_2$, $s = 1, 2$.

The assumption that the core potential is here connected with the division of sheer translational effects arising from the isotropic short-range strength forces and the effects resulting from the anisotropic potential part.

Thus, a core potential V_0 of the from

$$V_0(t) = \frac{d}{r^k(t)} \tag{20}$$

is taken, where d is the strength parameter and k is the steepness parameter. The above potential has been assumed by Srivastava and Zaidi [24] in view of the cutoff impact parameter in Anderson's theory [25].

As is known the S operator can be defined in terms of the time development operator:

$$S = U(+\infty, -\infty), \tag{21}$$

where the development operator $U(t, -\infty)$ satisfied the Schrödinger equation with the potential $V_1(t)$

$$i\hbar \frac{d}{dt} U(t, -\infty) = e^{\frac{iH_0 t}{\hbar}} V_1(t) e^{-\frac{iH_0 t}{\hbar}} U(t, -\infty), \tag{22}$$

and

$$V(t) = V_0(t)+V_1(t). \tag{23}$$

The development operator $U(t, -\infty)$ may also be written as

$$U(t, -\infty) = \exp\left(-\frac{i}{\hbar}\int_{-\infty}^{t} dt' e^{\frac{iH_0 t'}{\hbar}} V_0(t') e^{-\frac{iH_0 t'}{\hbar}}\right) U_1(t, -\infty). \tag{24}$$

Now, it is assumed that the operator V_0 does not operate on the internal states although it does depend parametrically [6]. Thus the matrix S may be given as the product

$$S = S_0 \times S_1, \tag{25}$$

where

$$S_0 = \lim_{t\to\infty} \exp\left(-\frac{i}{\hbar}\int_{-\infty}^{t} V_0(t')dt'\right), \tag{26}$$

and

$$S_1 = \lim_{t\to\infty} P\exp\left(-\frac{i}{\hbar}\int_{-\infty}^{t} e^{\frac{i}{\hbar}H_0 t'} V_1(t') e^{-\frac{i}{\hbar}H_0 t'} dt'\right). \tag{27}$$

As in [24, 26] the S_0 matrix is going to be treated nonperturbatively while the S_1 matrix is going to be developed into the expansion up to the second order perturbation calculus under the assumption that the operator $V_1(t)$ commutes with itself at a different time. We obtain as a result

$$S_1 = 1 - iS_1^{(1)} - \tfrac{1}{2}[S_1^{(1)}]^2, \tag{28}$$

where

$$S_1 = \frac{1}{\hbar}\int_{-\infty}^{\infty} e^{\frac{i}{\hbar}H_0 t'} V_1(t') e^{-\frac{i}{\hbar}H_0 t'} dt'. \tag{29}$$

Making use of the above assumptions the diagonal part of the velocity-dependent relaxation operator can be expressed by the formula

$$\Phi(p_{0z}) = i\frac{2\pi n}{(2j_a+1)}\langle p(\int_0^{\infty} 2\pi b db(S_0 - 1 - iS_0 \sum_m \langle j_a m\alpha|S_1^{(1)}|j_a m\alpha\rangle$$

$$-\tfrac{1}{2}S_0 \sum_{mm'}\sum_{\alpha' j_a'} \langle j_a m\alpha|S_1^{(1)}|j_a' m'\alpha'\rangle \langle j_a' m'\alpha'|S_1^{(1)}|j_a m\alpha\rangle)\rangle_{\perp,\mathrm{av}}. \tag{30}$$

The matrix elements which appear in the above equation can be evaluated in terms of the vector addition coefficients and modified Bessel function.

Thus from the multipole interaction (17) we get the following dependencies

$$\langle\sum_m \langle j_a m\alpha|S_1^{(1)}|j_a m\alpha\rangle\rangle_{\perp,\mathrm{av}} = \frac{(2j_a+1)\mu}{pb^l} F^l(j_a), \tag{31}$$

where the function $F^l(j_a)$ is supplied by

$$F^l(j_a) = \sum_{l_1 l_2} \frac{\tilde{C}_l(l_1 l_2)}{4\pi}\left(\frac{(2l_1+1)(2l_2+1)}{4\pi}\right)^{\frac{1}{2}} \begin{pmatrix} l_1 & l_2 & l \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} j_a & l_1 & j_a \\ 0 & 0 & 0\end{pmatrix}$$

$$\times \sum_{j_2} \varrho(j_2)(2j_2+1) \sum_{mm_2} (-1)^{m+m_2} \begin{pmatrix} j_a & l_1 & j_a \\ -m & 0 & m\end{pmatrix}\begin{pmatrix} j_2 & l_2 & j_2 \\ -m_2 & 0 & m_2\end{pmatrix}\begin{pmatrix} j_2 & l_2 & j_2 \\ 0 & 0 & 0\end{pmatrix}, \tag{32}$$

where $\varrho(j_2)$ stands for the population factor state j_2 and $\tilde{C}_l(l_1, l_2)$ is given by

$$\tilde{C}_l(l_1, l_2) = C_l(l_1, l_2)\left(\frac{2l+1}{16}\right)^{\frac{1}{2}} \frac{\Gamma(l+1)}{\Gamma(l+\frac{1}{2})} \sum_{k=0}^{l} \frac{(-1)^k \Gamma(l+2k+\frac{1}{2})}{(l+2k)\Gamma(l+2k)}. \tag{33}$$

Here Γ is a Γ-function. In the second order approximation the matrix elements of the operator are expressed by:

$$\left\langle \sum_{j_a'} \sum_{mm'} \langle j_a m\alpha|S_1^{(1)}|j_a' m'\alpha'\rangle \langle j_a' m'\alpha'|S_1^{(1)}|j_a m\alpha\rangle \right\rangle_{\perp,\mathrm{av}} = \frac{(2j_a+1)\mu^2}{p^2 b^{2l}} G(j_a, \omega\tau), \tag{34}$$

where the function $G^l(j_a, \omega\tau)$ is included in the formulae

$$G^l(j_a, \omega\tau) = \frac{1}{16\pi^3} \sum_{l_1 l_2} C_l^2(l_1, l_2) \sum_{j_a' j_2 j_2'} \varrho(j_2)\,(2j_a+1)$$

$$\times \begin{pmatrix} j_a & l_1 & j_a' \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} j_2 & l_2 & j_2' \\ 0 & 0 & 0 \end{pmatrix}^2 \sum_{\mu} \frac{1}{(l-\mu)!(l+\mu)!} (\omega\tau)^{2l} K_\mu^2(\omega\tau), \tag{35}$$

where

$$\omega = 2\pi c B(j_a(j_a+1) - j_a'(j_a'+1) + j_2(j_2+1) - j_2'(j_2'+1)). \tag{36}$$

Here K is a modified Bessel function, ω is the frequency corresponding to the energy transferred from translational to rotational motion, $\tau = b/v$ is the duration of the collision, B is a rotational constant, c is the speed of light.

Because of the $G^l(j_a, \omega\tau)$ is a slowly varying function of τ, the essential simplifying of the problem is possible here [27]. Consequently we put:

$$G^l(j_a, \omega\tau) = G^l(j_a, \omega\bar{\tau}), \tag{37}$$

where $\bar{\tau}$ is the average duration of the collision. Then with $\Gamma_a(p_{0z})$ taken as the imaginary part of (30) we obtain

$$\Gamma_a(p_{0z}) = \frac{2\pi n}{2j_a+1} \left\langle p \left(\int_0^\infty b db \left(\cos \frac{\eta}{b^{k-1}} - 1 \right) \right. \right.$$

$$\left. \left. + \frac{(2j_a+1)\mu^2}{p^2 b^{2l}} F^l(j_a) \sin\left(\frac{\eta}{b^{k-1}}\right) - \tfrac{1}{2} \frac{(2j_a+1)\mu^2}{p^2 b^{2l}} G^l(j_a, \omega\bar{\tau}) \cos\left(\frac{\eta}{b^{k-1}}\right) \right) \right\rangle_\perp, \tag{38}$$

where η is represented by

$$\eta = \sqrt{\pi} \frac{\mu d}{p} \frac{\Gamma\left(\frac{k-1}{2}\right)}{\Gamma\left(\frac{k}{2}\right)}. \tag{39}$$

As seen in (38) due to the assumed core potential and (25) this expression can be integrated analytically over the impact parameter b.

Thus finally the velocity dependent half-width line is the following

$$\Gamma_a(p_{0z}) = \frac{\pi n}{2j_a+1}\left\langle p\left(\eta^{\frac{2}{k-1}}\Gamma\left(\frac{k-3}{k-1}\right)\sin\left(\frac{\pi}{2}\,\frac{k-3}{k-1}\right)\right.\right.$$

$$-\frac{2(2j_a+1)}{(l-2)}\left(\frac{\mu}{p}\right)\eta^{-\frac{l-2}{k-1}}\Gamma\left(1+\frac{l-2}{k-1}\right)\sin\left(\frac{\pi}{2}\,\frac{l-2}{k-1}\right)F^l(j_a)$$

$$\left.\left.-G^l(j_a,\,\omega\bar{\tau})\,\frac{2(2j_a+1)}{(2l-2)}\left(\frac{\mu}{p}\right)^2\eta^{-\frac{2l-2}{k-1}}\Gamma\left(1+\frac{2l-2}{k-1}\right)\cos\left(\frac{\pi}{2}\,\frac{2l-2}{k-1}\right)\right)\right\rangle_{\perp}, \tag{40}$$

where l must satisfy the condition

$$2 < l < k+1. \tag{41}$$

Formula (13) together with (40) determines the shape of the rotational spectrum line within the Doppler limit according to the multipole and core potential parameters.

General equation (40) is true for the higher than dipole-dipole range of interactions. The first component in (40) contributes to the line shape coming from the relaxation velocity. The other two components show the interference effect between the translational and internal degrees of freedom.

Equations (13) and (40) are convenient for numerical calculations since they can be easily integrated over the respective momentum components of the radiator, the perturber and the relative motion.

Subsequently, the application of the theory to the calculation of the self broadened collision widths of rotational Raman lines for such molecules as N_2 and CO_2 will be taken into account in the next paper. Specifically, from comparison of theory with experiment one may hope to obtain some information about the short range interaction.

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APPENDIX

The spectral line shape $I(\omega)$ in impact approximation for multipole transitions for nonoverlapping lines is given by

$$I(\omega) = \sum_{\substack{JJ'\\MM'}}\sum_{if}\varrho_i\,\frac{\langle f\|X^{JM}\|i\rangle^*\langle i\|X^{J'M'}\|f\rangle}{\sqrt{(2J+1)\,(2J'+1)}}\,I^{J'M'}_{JM}(\omega-\omega_{if}), \tag{A1}$$

where $\langle i||X^{JM}||f\rangle$ are reduced matrix elements of a multipole J-th-order tensor operator X^{JM} for 2^J-pole interaction with radiation, M indicates particular one $(2J+1)$ irreducible components of the operator and $I^{JM}_{J'M'}(\omega-\omega_{if})$ is a line shape function which in Liouville

space notation is given by

$$I_{JM}^{J'M'}(\omega-\omega_{if}) = \frac{1}{\pi}\,\mathrm{Im}\int d_3\vec{p}_0\varrho^{\frac{1}{2}}\left(\frac{p_0}{2m_0}\right)\int d_3\vec{p}_0'\varrho^{\frac{1}{2}}\left(\frac{p_0'}{2m_0}\right)$$

$$\times\left(e_{if}(\vec{\kappa}\vec{p}_0JM),\ \frac{1}{\omega-\omega_{if}-\hat{h}_0-\hat{\Phi}}\,e_{if}(\vec{\kappa}\vec{p}_0J'M')\right). \tag{A2}$$

Here eigenvectors $e_{if}(JM)$ of the radiator internal energy are defined by the relation

$$e_{if}(JM) = \sum_{m_im_f}(-1)^{j_f-m_f}(2J+1)^{\frac{1}{2}}\begin{pmatrix} j_f & J & j_i \\ -m_f & M & m_i\end{pmatrix}|v_fj_fm_f\rangle\langle v_ij_im_i|, \tag{A3}$$

and the eigenvectors $e_{if}(\vec{\kappa}\vec{p}_0)$ of the Liouville space of the kinetic energy operator $\hat{h}_0$ of radiator are given by

$$\hat{h}_0e_{if}(\vec{\kappa}\vec{p}_0) = \left(\frac{\vec{p}_0\vec{\kappa}}{m_0}+\frac{\kappa^2}{2m_0}\right)e_{if}(\vec{\kappa}\vec{p}_0). \tag{A4}$$

The molecular operator relaxation $\hat{\Phi}$ is defined when it operates on the eigenvectors $e_{if}(\vec{\kappa}\vec{p}_0JM) = e_{if}(JM)\,e_{if}(\vec{\kappa}\vec{p}_0)$ as follows

$$\hat{\Phi}e_{if}(\vec{\kappa}\vec{p}_0JM) = \frac{n\Omega}{(2\pi)^3}\,Q\left(\frac{p_1^2}{2m_1}\right)\Big\langle\Big(\int d_3\vec{p}_1e^{-\beta\frac{p_1^2}{2m_1}}\sum_{\substack{j_ij_i'j_fj_f'\\J'M'}}\sum_{\substack{m_im_f\\m_i'm_f'}}(-1)^{j_f+j_f'-m_f-m_f'}$$

$$\times((2J+1)(2J'+1))^{\frac{1}{2}}\begin{pmatrix} j_f & J & j_i \\ -m_f & M & m_i\end{pmatrix}\begin{pmatrix} j_f' & J' & j_i' \\ -m_f' & M' & m_i'\end{pmatrix}(\langle j_i'm_i'v_i\vec{p}\alpha|T|j_im_iv_i\vec{p}\alpha\rangle$$

$$\times\delta_{m_fm_f'}\delta_{j_fj_f'}-\langle j_f'm_f'v_f\vec{p}\alpha|T|j_fm_fv_f\vec{p}\alpha\rangle^*\delta_{m_im_i'}\delta_{j_ij_i'})e_{if}(\vec{\kappa}\vec{p}_0J'M')$$

$$+\frac{i}{2\pi^2}\sum_{\alpha'}\int d_3\vec{p}_1\int d_3\vec{p}_1'\int d_3\vec{p}_0'e^{-\beta\frac{(p_1^2+p_1'^2)}{4m_1}}\delta(\vec{P}-\vec{P}')$$

$$\times\langle j_fm_fv_f\vec{p}\alpha|T|j_f'm_f'v_f\vec{p}'\alpha'\rangle^*\delta(\varepsilon-\varepsilon')\langle j_im_iv_i\vec{p}\alpha|T|j_i'm_i'v_i\vec{p}'\alpha'\rangle e_{if}(\vec{\kappa}\vec{p}_0'J'M'))\Big\rangle_{\mathrm{av}}, \tag{A5}$$

where Ω denotes the volume of the system.

When the matrix element of the above relaxation operator is constructed, the isotropy of the system would be taken into consideration. Following this matrix element Eq. (2) is obtained.

Formulae (2) and (A1) describe the interrelation between the Doppler and pressure broadening of a line, in the whole pressure region of interest. In particular, in the Doppler limit i. e. when the mean change of the Doppler shift $\vec{\kappa}(\vec{p}_0-\vec{p}_0')/m_0$ is greater than Π_{if},

the line shape function $I_{JM}^{J'M'}(\omega-\omega_{if})$ can be expanded into a series of the Π_{if} operators as follows:

$$I_{JM}^{J'M'}(\omega-\omega_{if}) = \int d_3\vec{p}_0 \varrho^{\frac{1}{2}}\left(\frac{p_0^2}{2m_0}\right)\tilde{I}^{00}(\omega-\omega_{if};\vec{p}_0) - \int d_3\vec{p}_0\varrho^{\frac{1}{2}}\left(\frac{p_0^2}{2m_0}\right)$$

$$\times \int d_3\vec{p}_0'\varrho^{\frac{1}{2}}\left(\frac{p_0'^2}{2m_0}\right)\tilde{I}^{00}(\omega-\omega_{if};\vec{p}_0)\Pi_{if}(JM\vec{p}_0; J'M'\vec{p}_0')\tilde{I}^{00}(\omega-\omega_{if};\vec{p}_0), \qquad \text{(A6)}$$

where $\tilde{I}^{00}(\omega-\omega_{if};\vec{p}_0)$ is the eigenvalue of the diagonal part of resolvent operator which is independent of J and M.

In the first order approximation when the imaginary part of (A6) is used, a velocity dependent Voigt profile is obtained which appears in text as formula (7).

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