

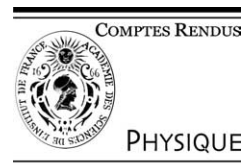


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Gas phase molecular spectroscopy/Spectroscopie moléculaire en phase gazeuse

Collisional effects on spectral line-shapes

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Presented by Guy Laval

Abstract

The growing concern of mankind for the understanding and preserving of its environment has stimulated great interest for the study of planetary atmospheres and, first of all, for that of the Earth. Onboard spectrometers now provide more and more precise information on the transmission and emission of radiation by these atmospheres. Its treatment by 'retrieval' technics, in order to extract vertical profiles (pressure, temperature, volume mixing ratios) requires precise modeling of infrared absorption spectra. Within this framework, accounting for the influence of pressure on the absorption shape is crucial. These effects of inter-molecular collisions between the optically active species and the 'perturbers' are complex and of various types depending mostly on the density of perturbers. The present paper attempts to review and illustrate, through a few examples, the state of the art in this field. This is to be related with the increasing quality of laboratory or onboard instruments (frequency difference laser, Fourier transform, diode laser spectrometers, . . .) which nowadays provide data of precision far above than what could be achieved ten years ago. **To cite this article:** *C. Boulet, C. R. Physique 5 (2004).*

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Résumé

Effets collisionnels sur les profils spectraux. La préoccupation croissante de l'humanité pour la compréhension et la sauvegarde de son environnement a engendré un regain d'intérêt scientifique pour l'étude des atmosphères planétaires à commencer par celle de notre Terre. Les spectromètres embarqués fournissent des informations de plus en plus précises sur la transmission et l'émission de rayonnement par ces atmosphères. Leur traitement par « inversion », dans le but d'extraire les profils verticaux (pression, température, fractions molaires), demande une modélisation précise des spectres d'absorption infrarouge. Dans ce cadre, la prise en compte de l'influence de la pression sur les profils est généralement cruciale. Ces effets des collisions inter-moléculaires entre l'espèce optiquement active et ses « perturbateurs » sont multiples et complexes et dépendent, pour l'essentiel, du domaine de densité des partenaires de collision. Cet article se propose d'illustrer et de passer en revue, à travers quelques exemples, l'actualité de ce domaine de recherche. Cet état des connaissances théoriques est à relier à la qualité croissante des dispositifs de laboratoire ou embarqués (lasers à différence de fréquences, spectromètres à transformée de Fourier et à diode laser, . . .) qui fournissent aujourd'hui des données d'une précision sans commune mesure avec ce qui était accessible il y a encore une dizaine d'années. **Pour citer cet article :** *C. Boulet, C. R. Physique 5 (2004).*

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Mots-clés : Line shapes ; Collisions ; Spectra

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1. Introduction

In order to calculate the absorption or diffusion of radiation in many practical systems, such as planetary atmospheres, combustion media, etc. one needs not only the positions and intensities of individual optical transitions, but also the spectral shape. This is of particular importance in spectral regions far away from band centers. As shown in Figs. 1 and 2, knowledge of the far wings of air-broadened line shapes for H_2O and CO_2 is essential to the accuracy of satellite retrievals [1]. Nearby resonances, the shape of isolated transitions is often described under atmospheric pressures in terms of the pressure broadened half-width γ and line-shift δ of the Lorentz profile. Both γ and δ depend on the intermolecular potential inducing various

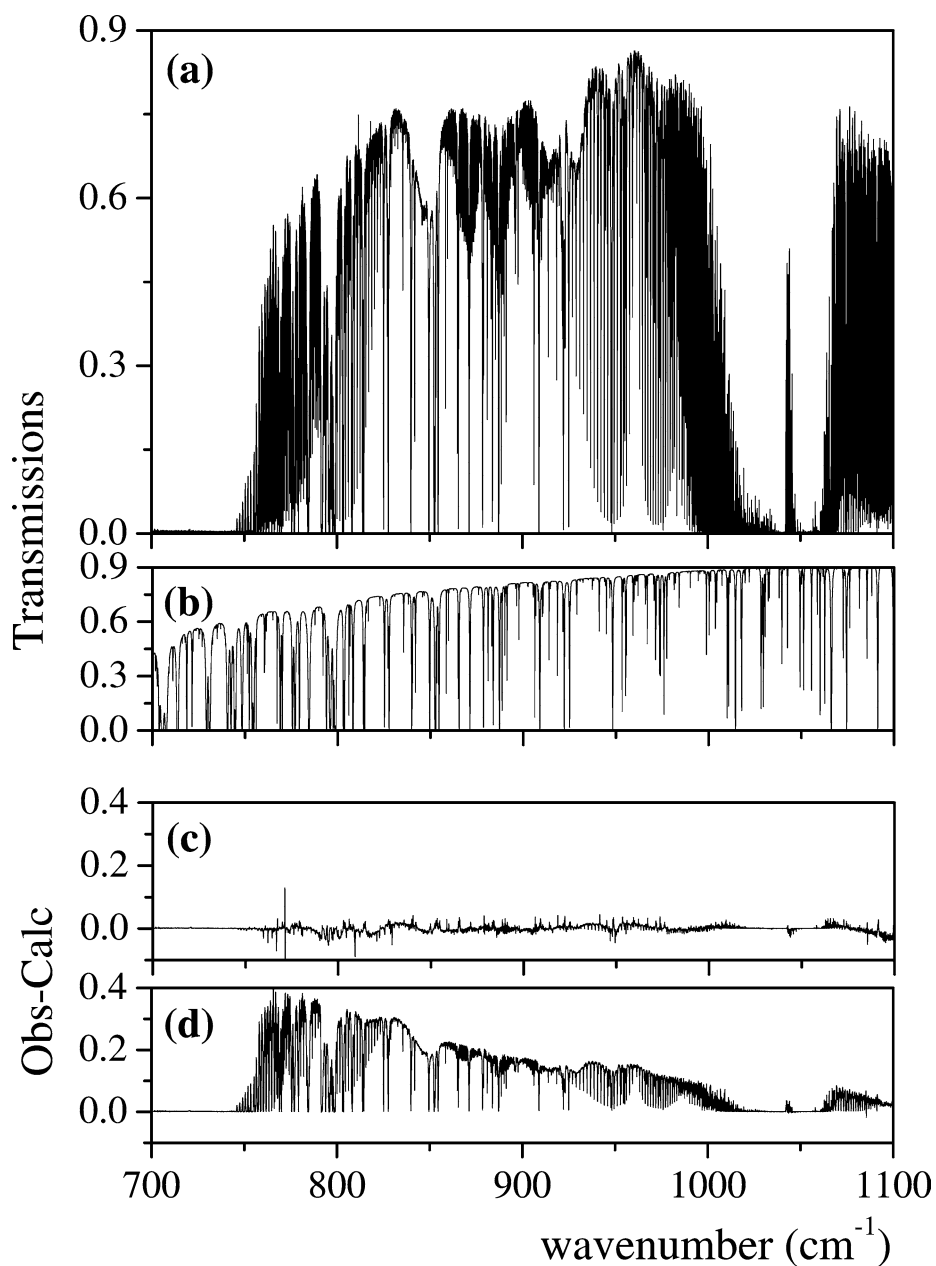


Fig. 1. Comparisons between measured and calculated atmospheric transmission spectra in high frequency wing of the ν_2 band of CO_2 [1]. (a) Measured spectra from ground with an elevation angle of 4.7° ; (b) calculated contribution of H_2O absorption; (c) and (d) measured-calculated deviations obtained with models respectively accounting for and neglecting collisional line-mixing between CO_2 lines.

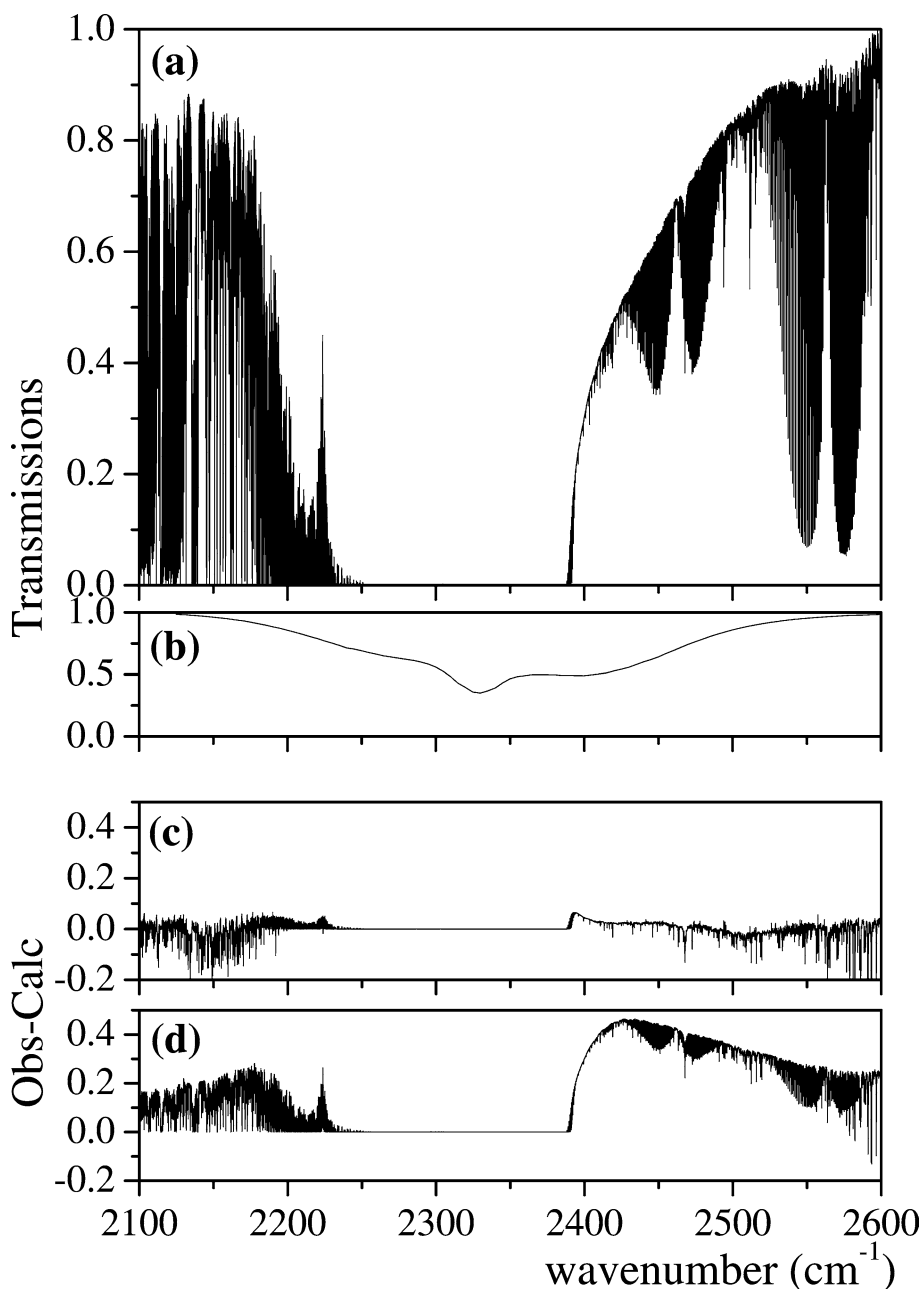


Fig. 2. Comparisons between measured and calculated atmospheric transmission spectra in the region of the ν_3 band of CO_2 [1]. (a) Measured spectra from ground with an elevation angle of 44.4° ; (b) calculated contribution of N_2 collision induced absorption; (c) and (d) measured-calculated deviations obtained with models respectively accounting for and neglecting collisional line-mixing between CO_2 lines.

collisional processes taking the radiating molecule from a rovibrational level to another one. Combined use of both measured and calculated values has led, in most cases, to more and more accurate values of the line shape parameters γ and δ stored in the spectroscopic data bases [2,3]. When the spectral separation between two transitions is smaller than their pressure broadened widths, the lines overlap and interferences may play a significant role leading to a more complicated spectral shape. For pressures in the atmospheric range, these line-mixing effects significantly affect the shape of Q branches and of closely spaced manifolds. Coming back to the window regions, i.e., far from band centers, the additional mechanism of collision induced absorption can make a contribution to the spectra, through the transient dipole that is induced during binary collisions. As illustrated in Fig. 2, the fundamental N_2 band near $4.3 \mu\text{m}$ participates significantly to radiative processes in the atmosphere of the Earth.

Although the determination of accurate profiles for molecular vibration–rotation transitions valid over wide ranges of different physical parameters (e.g., number density, temperature, spectral detuning) remains an unsolved problem,¹ substantial progress has been made in the past decades towards accurate calculation of absorption profiles. The purpose of this paper is to describe some of these works and present, with no claim to completeness,² a review of studies devoted to collisional effects on the absorption shape. It is hoped that our bibliography will give the reader the starting point for a more detailed analysis of previous works, including the more historic ones.

2. Lorentz profile: pressure broadened widths and shifts

Let us consider, as a first step, the shape of non-overlapping lines at atmospheric densities, for small frequency displacements from the centers of the transitions. In this case, use of both the binary collisions and impact approximations, where the duration of collisions is assumed to be zero, leads to the usual Lorentzian profile, written in terms of the half width γ and shift δ . Various *tractable* theories have been proposed for the calculation of these line parameters, depending on the degree of complexity of the collisional partners.

For systems of practical interest, which involve molecule–molecule collisions, the most commonly used formalism is the ‘ultimate’ version of the Anderson–Tsaio–Curnutte theory as proposed by Robert and Bonamy (RB) in the 1980s. A full description of this formalism can be found in [6], and only the salient features are recalled here. The relative translational motion is treated classically, so that the particles are assumed to follow classical trajectories determined by the isotropic part of the intermolecular potential. The internal states of the molecules (vibration and rotation) are treated quantum mechanically and the width and shift cross-sections are expressed in terms of the scattering matrix S . In the RB formalism, S is calculated to all orders in the interaction potential, thus insuring its unitarity through linked cluster techniques. At the same time, short range contributions to the anisotropic part of the potential have been included. This has led to a better description of pressure broadening in systems in which these collisions are efficient, for instance when electrostatic interactions are weak. In recent years, calculations based on this formalism have become very numerous and cannot be detailed here. Nevertheless, the reader will find examples of applications of the original RB model to linear, symmetric top, and asymmetric-top molecules in [7–12]. Among the recent improvements that have been made to the RB formalism, let us mention the formulation of Neshyba and Gamache [13,14]. It allows analysis of the truncation of the development of the intermolecular potential in terms of the centers of mass separation, since sufficient order needs to be included to achieve convergence of calculated cross-sections. On the basis of such a refined and fully complex formalism, subtle effects can now be analyzed like the vibrational dependence of the N₂ broadened line widths and shifts of H₂O [15]. In recent years, particular attention has also been given to pressure broadening (and shifting) coefficients of CH₄ lines since methane is present in our atmosphere and in most of giant planets and is involved in the global warming problematic. Therefore the RB formalism has been extended to spherical tops by using a fully symmetrized tensorial form of the various transition moments so that realistic eigenfunctions, corresponding to the polyad structure, can be incorporated in the calculations. Various applications to CH₄ may be found starting from [16–18]. Finally, in the RB formalism, the trajectory is usually approximated through a limited development around the distance of closest approach leading, for instance, to the ‘parabolic’ modeling introduced in [6]. However, the influence of the trajectory description needed to be more carefully analyzed. The rigorous solution of the classical dynamics equations for the trajectory has been first introduced in the RB formalism by Bykov et al. [19] and later on generalized by Buldyreva et al. [20,21]. On that basis the limits of validity of more approximate descriptions are now better understood.

When the colliding particle is an atom, it is possible to use a numerical solution of the time dependent Schroedinger equation to obtain the semi-classical S matrix. This approach proposed by Neilsen and Gordon [22] has been recently tested by comparisons with extensive fully quantal calculations (see later) and recent measurements of HF-Argon [23] and HCl-Argon [24] widths and shifts, showing good agreement with both the close-coupling and experimental results. Due to its computational ease, this model appears as a practical and reliable tool for the investigation of specific features, as a preliminary step before fully quantal calculations. It has been used for instance in [23] to demonstrate that vibration–rotation coupling contributes to the rotational dependence of both widths and shifts in HF-Argon.

For molecule–atom systems, the great increase of computational capabilities in the last two decades now allows the development of ‘essentially exact’ calculations, within the full quantum treatment proposed by Shafer and Gordon [25]. However these ‘close coupling’ calculations of the quantum coupled channel equations to obtain the S matrix are very time consuming. Consequently, there has been great interest in the development of approximate methods reducing the dimensionality of the problem. Among the various decoupling approximations, let us only mention the widely used coupled states (CS) scheme

¹ Even if the general frame of pressure broadening has been established a long time ago [4,5].

² A complete coverage of even only the recent papers in the field is, of course, not attempted.

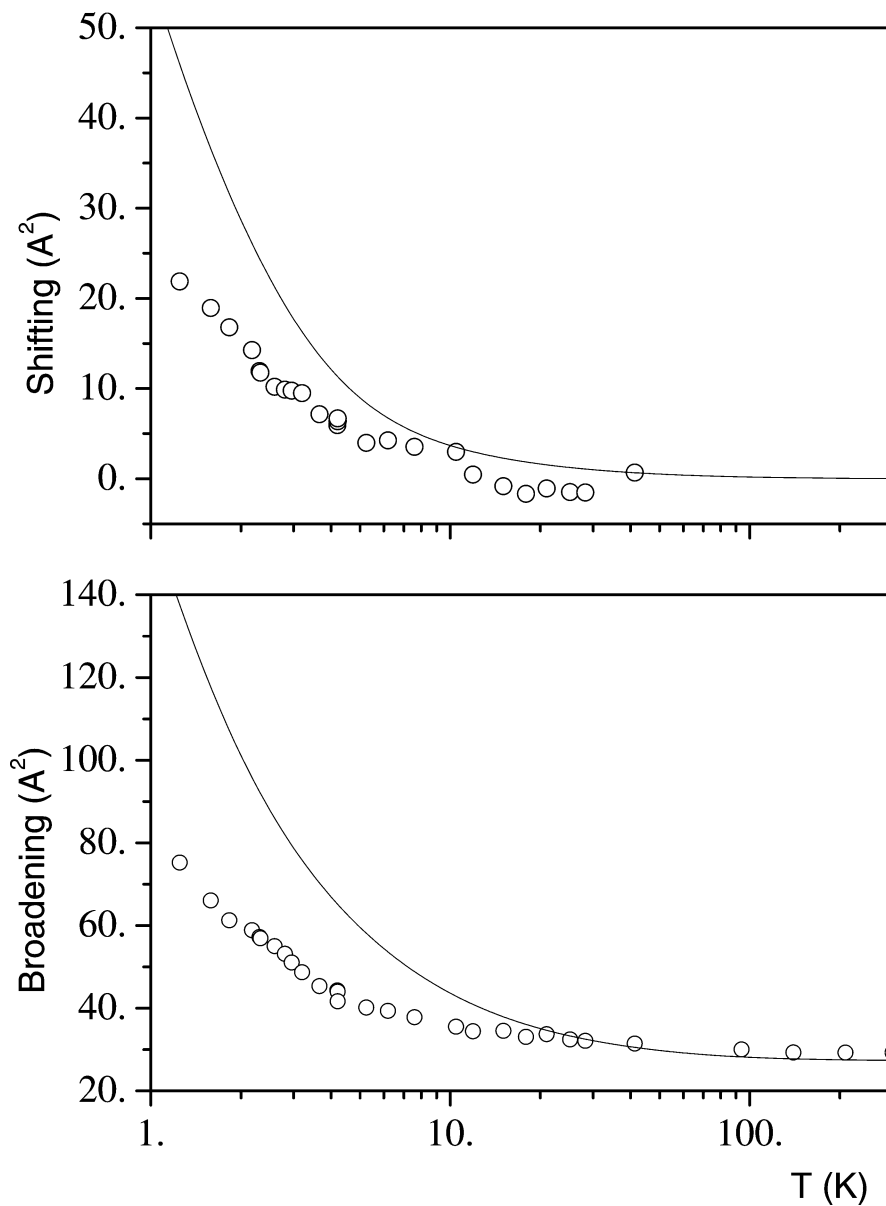


Fig. 3. Comparisons between measured (symbols) and CC calculated (lines) broadening and shifting cross sections of the $R(0)$ line of the 1-0 band of ^{12}CO versus temperature [39].

of Mc Guire and Kouri [26]. The region of validity of this approximation is now fairly well understood [27–29] and CC and CS calculations have been made for many atom–molecule systems, thanks to the availability of two quantum dynamical codes: MOLCOL [30] and principally MOLSCAT [31]. Subtle effects can now easily be analyzed. Let us mention the decomposition [32] of the shifts observed in the fundamental band of CO in He and Argon into parts odd and even in the line number m , which is a powerful tool for separating the relative contributions of the isotropic and anisotropic part of the potential. More generally, it can be stated that for cases in which accurate intermolecular potentials exist, theoretical line broadening and shifting cross-sections agree with experiment to a few percent over a wide range of physical conditions (temperature dependence, vibrational dependence, etc.) [33–35], with a noticeable exception: the very low temperature domain, where He (H_2)-broadened profiles can be measured in cryogenic mixtures prepared by the collisional cooling techniques. Severe disagreements between experiment and theory have then been observed [36–39], as illustrated in Fig. 3, the origin of which is not clearly understood: quality of the potential energy surface, validity of the impact approximation, problems with the experiment, In any case, this problem deserves further investigation.

3. Line mixing in the impact limit

At perturber pressures where lines are broadened enough to overlap, collisions can transfer intensity among them, profoundly altering the spectral shape [40,41]. Most of the work in this area has been motivated by the need of modeling profiles for two problems of practical importance. The first is use of coherent Raman spectroscopy as a tool to determine temperature and composition in flames and combustion engines which has required an accurate model for the Raman Q branch of N_2 [42]. The second application concerns CO_2 which is the constituent most commonly used for (satellite) IR remote sensing of the temperature profile of the Earth's atmosphere. As is now well known, an accurate description of the Q branch lines of the numerous bending bands of CO_2 perturbed by N_2 and O_2 is required [43]. Rotational lines in Q -branches are closely spaced and therefore, since they extend over small spectral ranges (a few 10th of cm^{-1}), the impact approximation can be used to construct the relaxation matrix W that describes line-mixing. For isolated lines, only the diagonal elements [$\gamma_n - i\delta_n \equiv W_{nn}$] are required. When the lines overlap, the off-diagonal rotational elements describing all the coupling between lines have no more negligible effects and must be accounted for to describe the vibrational band as a whole.

For atomic perturbers, within the impact approximation, the entire relaxation matrix can be calculated with almost no more effort than is required for the diagonal elements. Indeed, in a fully quantum treatment, a code like MOLSCAT [31] provides a complete set of S matrices, the appropriate combinations of which then provide either diagonal or off-diagonal cross-sections. In the past few years, the Raman Q -branch of CO perturbed by He and Ar has been the subject of detailed experimental and theoretical investigations [29,44]. In this case the CC formalism leads to a consistent description of the line coupling mechanisms, but some experimental features remain unexplained like the Ar-broadened profile at low temperature [29]. However the main interest of such 'first principles calculations' is that they enable tests of more approximate methods which are still required for perturbers of practical importance – such as N_2 or O_2 for the Earth's atmosphere.

Various approaches have been proposed for the modeling of line mixing for complex systems: they include very simple empirical approaches [45], and the use of fitting [46] and scaling [47,48] laws. The scaling approach based on the Energy Corrected Sudden (ECS) approximation introduced by De Pristo et al. [49] in the infinite order sudden model of Green [50,51] has been widely and successfully used for a number of systems. This model allows to express the entire relaxation matrix, for a given vibrational band, in terms of a limited 'fundamental' set of parameters (usually the excitation cross sections out of the fundamental rotational level $\sigma(0 \rightarrow j, T)$). These quantities can be determined either from calculations or deduced from measured data (pressure broadening cross-sections and/or Q branch profiles). In this last case, the basic rates are modeled through convenient analytical expressions based on parameters which are determined from fits of experimental data. Comparison between ECS predictions and accurate coupled channel scattering calculations, starting from the same potential, have shown that the ECS formalism includes, explicitly and intrinsically, the coupling of the various angular momenta involved in the problem (rotation–vibration–photon). Furthermore, the coupling cross-sections verify the detailed balance principle through an enforcing procedure proposed by De Pristo et al. [49]. Among the numerous applications of the ECS formalism, let us mention here the calculation of line-mixing effects in air broadened CO_2 Q branches. The approach proposed in [52] expresses the coupling between P , Q (if they are allowed) and R lines within vibrational bands of any symmetry [$\Sigma-\Sigma$, $\Sigma-\Pi$, $\Pi-\Pi$, $\Pi-\Delta$] in terms of a *unique* set of basic inelastic cross-sections and an effective duration of collision $\bar{\tau}_c(T)$. Comparisons with numerous CO_2 spectra measured both in the laboratory and the atmosphere have demonstrated the quality of this approach [53,54]. This success has been confirmed by similar studies in the case of N_2O [55]. A similar analysis of line mixing effects in NH_3 spectra based on an ECS approach extended to symmetric top molecule has been recently developed, covering various vibrational bands as well as various perturbers [56,57]. This study was motivated by the need of an accurate description of the NH_3 line shape for studies of planetary atmospheres or pollution monitoring.

For molecules like CH_4 or O_3 , of critical importance for atmospheric physics, due to their complex spectroscopic structures, more simple approaches are needed to model the profiles of spectral features (Q branch, P and R manifolds, clusters of lines) affected by line interference effects. In the approach developed in [58], the off-diagonal elements of the relaxation matrix are constructed starting from state-to-state rotational transfer rates. Most of these rates – those corresponding to the main channels – are computed from the intermolecular potential by using a semi-classical model. Connection between these state-to-state parameters and line coupling cross-sections is then made through a few empirical parameters which somehow account both for the influence of the types (P , Q , R) of the lines considered and the deficiency of the semi-classical calculation of the basic rates. Here again the ability of the model was confirmed by numerous comparisons between laboratory [58,59] as well as atmospheric spectra [60].

4. Band wings

Line-mixing effects are particularly important in the weak absorption regions: micro windows between rotational components, central gap of a vibrational band with no allowed Q branch, and the wings of vibrational bands. Wings (i.e.,

continuum) of H₂O and CO₂ vibrational bands are of practical importance since they define most of atmospheric transmittance windows [61–64]. It is now well recognized that an accurate specification of the H₂O continuum absorption is essential [61] to the accuracy of satellite retrievals for any spectral region, i.e., from microwave to visible. It is also generally accepted that the major contribution to that continuum is due to the wings of the strongest lines of H₂O, even if water dimers and collision induced absorption may be present in specific conditions (spectral regions, ...). Similarly, most of the spectra produced by advanced infrared sounders are sensitive to the CO₂ line shape in the wings of both the ν_3 (4.3 μm) and ν_2 (15 μm) vibrational bands [62,63]. Note also that modeling the long path absorption in the atmosphere of Venus requires an accurate description of self-broadened CO₂ line wings at high temperature [64]. In recent years, substantial progress has been made and different tractable theories now exist, depending on the detuning from the most intense rotational components, and of course on the complexity of the active molecule and collision partner.

For moderate frequency displacements from the line centers, i.e., smaller than the inverse of the duration of the efficient collisions, the influence of the frequency dependence of the relaxation matrix, due to the breakdown of the impact approximation, will remain small. Therefore the impact models described above will give reliable results in this type of spectral region, named as ‘near-wing’ region (e.g., [1,52]). On the other hand, for large frequency displacements, corresponding to the far wings of allowed spectral lines, starting from the work of Rosenkranz [65,66], Ma and Tipping [67–71] have developed a theory based on the quasistatic and binary collision approximations. It leads to very satisfactory predictions for the infrared as well as the millimeter wave H₂O continua. In this section, we give a brief survey of some recent results obtained in this field, depending on the frequency detuning involved.

4.1. Near-wing calculations

4.1.1. CO–He

It is known from the early work of Bulanin et al. [72] that line interferences have considerable effects in the micro windows between high J rotational components, i.e., in the near wing of the CO fundamental band. In these regions, they lead to a strongly sublorentzian behavior. For a light perturber like He, leading to short collisions, the impact approximation may be thought to be sufficient. Consequently the Shafer–Gordon formalism and state of the art close coupled solutions of the scattering equations can be used to calculate an ab-initio relaxation matrix. However a recent comparison [73] between experiment and close coupling line shapes has demonstrated that the near wings are particularly sensitive to the accuracy of a sum rule. The latter connects, in the rigid rotor limit, the off-diagonal elements and the diagonal terms of the relaxation operator in the line space:

$$\frac{1}{d_k^{(1)}} \sum_l d_l^{(1)} W_{lk}(\omega) = -W_{kk}(\omega). \quad (1)$$

In this equation, $d_l^{(1)}$ is the reduced matrix element of the dipole operator and the sum should be extended to all lines l coupled to the given line k , excluding the term $k = l$. It has been shown in [73] that, due to the impact approximation, the Shafer–Gordon formalism, which is the ‘most exact impact model’, verifies only approximately the sum rule with differences around 10 to 15%. Unfortunately such discrepancies are too important for an accurate description of the near wing region. This shows that, even for a system like CO–He, the range of validity of the impact approximation is smaller than has been suspected. This result, already analyzed by Monchick et al. [74], suggests that off-the-energy-shell calculations of the off-diagonal elements are needed for distant lines. Since they are not yet available, the present alternative is to enforce the sum rule, for instance by calculating the off-diagonal elements through the Shafer–Gordon formalism and deducing the diagonal one by Eq. (1). However this result constitutes, paraphrasing Monchick [74], an impetus for off-shell molecular scattering calculations in the future.

4.1.2. CO₂–N₂

For such a system the a priori calculations of the whole relaxation matrix is still untractable. However, the ECS formalism respects intrinsically the sum rule, since the diagonal elements are calculated from Eq. (1). It may thus be reasonably expected that this model will satisfactorily reproduce the near-wing behavior as confirmed by recent results [52] in the near wing of the ν_2 band, up to about 150 cm^{-1} from the center. For larger detunings discrepancies appear, which may be due to the finite duration of collisions. However more accurate experiments in the very far wing are now needed to go further into the analysis.

4.2. Far wing calculations

As mentioned previously, most theoretical calculations in this field have been devoted to the water vapor continuum due to the far wings of strong absorption bands of H₂O separating the IR transmittance into several windows. The theoretical challenge was the following: is it possible to include simultaneously in the line-shape calculation: line coupling effects, the finite duration

of collisions leading to the frequency dependence of W , and statistical initial correlations which may be of some importance for detuning of the order of kT ? Ma and Tipping, in a series papers [67–71], have improved or eliminated many of the restrictions and assumptions of the original Rosenkranz quasistatic theory [65,66]. For the infrared spectral regions their theory works well for H_2O –(H_2O , N_2 , and CO_2) and gives satisfactory agreement with both laboratory data and atmospheric measurements. More recently its validity has been extended to the millimeter wave region by eliminating the band average approximation [68,71]. Finally, note that the same formalism was applied with success to the wing of the ν_3 fundamental band of pure CO_2 for temperatures between 218 and 751 K relevant to the conditions encountered in the deep atmosphere of Venus [75].

4.3. From resonance to the far wings

To our knowledge, no tractable theory allows ‘first principles’ calculations starting from the intermolecular potential for all spectral regions. However, an approximate model has been proposed by Kouzov [76] and improved by Bonamy and Buldyreva [77,78]. It is a generalization of the ECS approach to arbitrary frequency detunings, leading to a frequency dependent relaxation matrix which verifies all known general relations obtained from first principles and particularly the sum rule in Eq. (1). For small detuning it reduces to the traditional ECS impact model allowing the basic ECS rates to be identified. It has been applied with success to the description of the N_2 anisotropic depolarized spectrum [78] in the whole frequency range, up to the far wing where the quasi exponential decrease of the scattered light intensity versus frequency is well reproduced thanks to a convenient choice of the generalized adiabaticity factor. More recently the theoretical analysis of the anisotropic scattering spectrum of the ν_1 band of CO_2 was attempted on the basis of the same non-Markovian ECS formalism [79]. In this case, substantial inconsistencies between theory and experiment are found whose origin remains unexplained.

5. Beyond the impact approximation: another example

As already mentioned, the far wings of transitions for various molecular systems clearly demonstrate the need of lineshape formalisms that avoid use of the impact limit. Furthermore in some cases, the finite duration of collisions can also significantly affect the core region of lines for light molecules (HF , HCl) at moderate perturber densities. Measurements in the 0–1 and 0–2 bands of HCl in a bath of Argon have been recently made for Ar pressures between 10 and 50 atm [24]. Although the rotational components remain isolated from each other due to the high rotational constant B , significant deviations with respect to the impact behavior – i.e. an additive superposition of Lorentzian lines – grow as the Ar density increases. Among the processes affecting the core region of the rotational lines one has remained poorly analyzed : the intensities of the low J lines – as determined from fits of the observed spectra – show a significant linear decrease with increasing Ar pressure. Up to now, no definitive interpretation of this phenomenon exists but many possible mechanisms have been proposed. Kouzov et al. [80] have shown that the formation of HCl –Ar complexes leads to such a decrease of the intensities of the monomer rotational components. Since the complex equilibrium constant depends on J , the intensity is selectively transferred from the low J lines of the monomer spectrum to the bands of the complex. However, calculations from an accurate HCl –Ar potential energy surface show [24] that this mechanism alone cannot explain the observed decreases and that other processes likely contribute to this effect.

It has been shown in [24] that a significant part of the intensity decrease comes from the failure of the impact approximation. By neglecting line-mixing effects, the profile of a given rotational $f \leftarrow i$ component can then be written as

$$I_{fi}(\omega) = \frac{1}{\pi} \text{Re} \int_0^{+\infty} dt e^{-i(\omega - \omega_{fi})t} e^{-g_{fi}(t)}. \quad (2)$$

Since we consider moderate perturber densities, the line shape in the core region of any rotational component mainly depends on the $g_{fi}(t)$ function at times t significantly greater than the duration τ_c of efficient collisions. However, the asymptotic behavior of $g_{fi}(t)$ for times $t \gg \tau_c$, when taking into account the effect of the finite duration of collisions, must be written as:

$$\lim_{t \gg \tau_c} g_{fi}(t) = (\gamma_{fi} - i\delta_{fi})t + (a_{fi} - ib_{fi}), \quad (3)$$

where γ_{fi} and δ_{fi} , which are the usual impact width and shift of the transition, can be expressed in terms of S matrix elements and calculated, for instance, with the NG approach [22]. The constant term in Eq. (3) is a correction to the *usual impact behavior*. The parameters a_{fi} and b_{fi} , which characterize the effects of the finite duration of collisions on the line shape in the core region, can be expressed in terms of some specific evolution operators, which can also be determined from the same NG algorithm. Returning to Eq. (2), using Eq. (3) and assuming small values of a_{fi} and b_{fi} , the profile can then be written as:

$$I_{fi}(\omega) = \frac{1}{\pi} [1 - a_{fi}] \frac{\gamma_{fi} + b_{fi}(\omega - \omega_{fi} - \delta_{fi})}{\gamma_{fi}^2 + (\omega - \omega_{fi} - \delta_{fi})^2}. \quad (4)$$

This shows that the correction to the Lorentzian impact profile has an asymmetric dispersion shape, with an asymmetry parameter b_{fi} . Since a_{fi} is proportional to the perturber density and provided that its calculation leads to positive values, the factor $1 - a_{fi}$ appears as an ‘apparent’ intensity decrease. Note that this must be considered as a ‘line shape effect’ rather than a real decrease of the integrated intensity. In fact, since Eq. (4) is only valid in the core region, the shape in the resonance region exhibits a global attenuation when P_{Ar} increases, due to the frequency independent damping factor $1 - a_{fi}^0 P_{Ar}$. Meanwhile, the intensity is transferred in the wings of the rotational component, i.e., outside the region of used for the fit of the line in the measured spectra.

The γ_{fi} , δ_{fi} , a_{fi} , and b_{fi} parameters have been calculated for HCl–Ar [24] from an accurate potential using the NG classical path algorithm [22]. As already mentioned, the calculated widths and shifts agree well with the experimental data. Analysis of the measured spectra have shown that the asymmetry parameters are smaller than typically $\pm 10^{-3} \text{ atm}^{-1}$ and hence too small to be determined accurately from the experiments. The semi classical calculations, which are the first made for this parameter, confirm this smallness. Furthermore, the order of magnitude of the calculated damping factors are consistent with the observed experimental attenuations versus J . It is worth noting that these results are, to our knowledge, the first calculations of a finite duration effect in the core region of the lines. It can be concluded that a large part of the intensity decrease observed at low J results from the effect of the finite duration of collisions which is as significant as the complex formation previously invoked by Kouzov et al. [80].

6. Spectral line shape from the Doppler to the collisional regime

Let us now consider the ‘opposite’ domain of low perturber densities, i.e., significantly sub-atmospheric pressures. To analyze line profiles in this pressure range, the well known Voigt shape has been widely used, giving in most cases a reasonable fit of experimental data. However, there are now numerous high resolution infrared studies (e.g., [81–83]) which have pointed out discrepancies with respect to this profile. The intrinsic limits of the Voigt shape (no correlation between collisional and Doppler broadening) have been known for a long time [84], as well as the need to incorporate simultaneously in the theory, the reduction of the Doppler component by velocity changing collisions (Dicke effect) and speed inhomogeneous effects. CARS investigations of H_2 in binary and ternary mixtures have shown that the latter are of primary importance for an accurate description of the line shape since the lightness of the active molecule enhances the speed effects [85].

In other words, a complete description from the low density regime (Doppler) to moderately high densities (impact broadening) requires a model that treats collision effects and free flight simultaneously. Phenomenological approaches of increasing generality were successively introduced, first within the soft (Galatry [86]) and hard (Rautian and Sobelmann [87]) collision regimes, then by combining these two limit cases. Then velocity state or phase changing collisions were introduced as well as the possibility of partial statistical correlations between these different types of collisions (see [85,88–94] and references therein). These models have allowed the analysis of most of the very subtle line shapes which have been observed thanks to the development of ever more sophisticated techniques both in IR and Raman spectroscopies. Despite these gratifying results, one point remains worrying, which is clearly illustrated by the analysis of measurements of extremely high quality of the shape of the $v = 0 \rightarrow 1$, $j \rightarrow j \pm 1$ lines of trace amounts of HF in between 50 and 500 torr of Argon [82]. Fits of the observed profiles to a ‘convenient’ phenomenological line shape allow to determine optical diffusion coefficients which sometimes correlate well with ordinary diffusion coefficients and sometimes do not! A more recent re-analysis still leaves opened a number of dynamical phenomena [95]. This example suggests that ‘ab initio’ calculations of the line shape at low density, i.e., starting only from the interaction potential between the active molecule and its perturbers are clearly needed in order to elucidate the limits of the ‘standard’ profiles.

State of the art methods for calculating such ab-initio profiles from first principles are not so far advanced. Among them, the application by Demeio et al. [96] of the generalized Hess method (GHM) to the calculation of the above mentioned HF–Ar line shape must be emphasized. Agreement between predicted and measured profiles is generally quite satisfactory, suggesting the fundamental correctness of the approach which has moreover shed more lights on the phenomenological models previously used. In the GHM theory, the parameter characterizing Dicke narrowing is a weighted sum of the ordinary optical diffusion coefficient *and* of a pressure broadening contribution which is negligible for some rotational transitions but not for some others. Therefore GHM provides a possible explanation of the anomalous behavior of the ‘effective’ coefficients as deduced from the fits of measured spectra. Moreover, there is no distinction between velocity changing and phase changing collisions which are inretrievably intermixed in the GHM formalism, contrary to phenomenological models. In a more recent work devoted to CO–Argon, Wehr et al. [97] have demonstrated the need of a full numerical solution of the generalized Waldmann–Snyder equation in order to properly take into account statistical correlations between translational motion and the evolution of the optical coherence associated with the internal degrees of freedom.

7. Collision induced spectra

It is well known that gases that do not have a permanent (or vibrating) dipole moment absorb radiation in the IR and other spectral regions. This Collision Induced Absorption (CIA), which comes from the dipoles induced during collisions, consists in broad but resolved lines in the case of H_2 or D_2 and in unresolved bands of strongly overlapping lines for other molecules [98]. CIA is of considerable importance in astrophysics and planetology since, for instance, hydrogen is the most abundant constituent in the upper atmosphere of the outer planets. Coming back to Earth, as already mentioned, the collision induced fundamental bands of N_2 and O_2 are significant parts of the radiative processes in the atmosphere.

For such rather heavy molecular systems, calculations have been made within the isotropic potential approximation which neglects the anisotropy of the intermolecular energy surfaces. This approximation together with semi classical expressions of the matrix elements of the induced dipole as given by a multipole induction model, and use of the approximate Birnbaum–Cohen line shape, leads to substantial simplifications of the computational task and to a reasonable agreement with experiment, even if some problems remain in the description of the wings [99,100].

For systems such as H_2 – H_2 or H_2 –He, most of these approximations can be avoided. Ab initio induced dipole moments can be calculated with highly correlated wave functions [101]. Then ‘rigorous’ fully quantum calculations of the CIA profiles have been made by numerical integration of the close coupled Schrödinger equation, with a frame commonly called ‘radiative close coupling scheme’ since it includes the quantized radiation field in the Hamiltonian [102]. This approach allows one to account for the anisotropy of the intermolecular potential. This has been done recently for H_2 colliding with He, H and H_2 [102], showing that the effects of the anisotropy originate mainly from interferences between the various dipole components. On that basis, other mechanisms need now to be investigated like rotational mixing in H_2 – H_2 CI scattering. Of course, calculations which account for the anisotropy of the potential allow ‘intrinsically’ the analysis of the contributions of bound pairs (Van Der Waals molecules) which cause sharp spectral features that can be observed at low temperatures. Finally, it must be emphasized that such ab initio calculations, here again, are essential to a better understanding of the reliability of more approximate methods. The latter are essential for more complex systems and needed for the accurate *and* efficient modeling of CIA in radiative transfer codes where absorption profiles must be ‘quickly’ computed for a variety of physical conditions.

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