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ON THE NATURE OF COLLISION-INDUCED ABSORPTION IN GASEOUS HOMONUCLEAR DIATOMICS

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Abstract—The phenomenon of collision-induced absorption in equilibrium gases is considered by accounting for the statistical–physical partitioning of bound, metastable and free bimolecular states. The importance of molecular anisotropy and dimers formation is emphasized. A line-mixing model is suggested to describe the overall collision-induced bandshapes of nitrogen and oxygen fundamentals, which effectively accounts for the perturbation of monomers rotational movement. Copyright © 1996 Elsevier Science Ltd

1. INTRODUCTION

Collision-induced absorption (CIA) spectra appear as weak and diffuse absorption bands in the spectral region of homonuclear diatomics fundamentals. Since their first detection by Welsh et al in 1949,[1] these bands have attracted a good wealth of attention from spectroscopists. This is in part due to the importance of these absorptions for the practical needs, albeit CIA is known to contribute significantly to transmission of radiation in the Earth's atmosphere,[2,3] as well as to play a crucial role in the radiation budget of the giant planets.[4] More important is that the study of this phenomenon enables one to achieve a better insight into the nature of intermolecular interactions. Moreover, during several decades the study and interpretation of CIA profiles served a unique instrument to characterize spectroscopically the so-called van der Waals dimers formation in the gas-phase. Nowadays the use of a much more advanced molecular beam technique in conjunction with high-resolution spectroscopic tools results in obtaining the wealth of information about van der Waals molecules (see, e.g., Refs. 5, 6). Thorough examination of collision-induced absorption phenomenon does not lose, however, its actuality.

It is a widely held belief that the induced absorption mechanism in the region of homonuclear diatomics fundamentals can well be described by considerations of the transient dipole moment occurring in the course of binary collisions. In the limit of low temperatures some additional contribution is waited for due to the formation of van der Waals dimers. The purely collisional nature of this phenomenon is emphasized by the most frequently employed term "collision-induced absorption".

The only undoubtful statement concerning the nature of CIA is, however, that it is due to binary intermolecular interactions. Explicit analysis is needed to establish whether these interactions result in formation of some bound or quasibound† bimolecular states or they leave interacting moieties unbound, thus keeping the purely elastic collisional nature of CIA intact. It is a detailed statistical mechanics consideration which is able to elucidate this problem. In Sec. 2 we shall briefly comment on how this can be done.

To model the CIA profile one has to consider the effect of rotational perturbations on the interacting moieties. This is performed in Sec. 3 by virtue of the line-mixing model, taking the spectra in the region of fundamentals in pure nitrogen and $O_2 + Ar$ mixture as an example.

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†Quasibound or metastable states are dimeric states with internal energy in excess of the dissociation limit. These states are capable of decaying spontaneously. Being formed in the pair scattering process they are conventionally called scattering resonances.

2. INTEGRATED INTENSITY

It is noteworthy to decompose an integrated intensity of CIA into free and bound + quasibound contributions. The total intensity I of absorption can be expressed in terms of the product of an averaged intensity of absorption per one molecular pair S_{ind} and a number of pairs N_p per unit volume of a gas at equilibrium:

$$I = \frac{1}{l} \int \alpha(\nu) \, d\nu = S_{ind} N_p / V. \tag{1}$$

Here $\alpha(\nu)$ is the coefficient of absorption, l is the length of absorbing layer, V stands for the gas volume. The total number of pairs can be easily estimated as:

$$N_p = \frac{N(N-1)}{2} \approx \frac{1}{2} N^2, \tag{2}$$

provided N stands for the total number of molecules in a gas. Note that only a fraction of pairs $x_{bm} = N_{bm}/N_p$ are in their bound or metastable states, the rest x_f must be considered as being in the course of elastic collision with a variety of impact parameters. There is much similarity between bound and quasibound states and therefore it is more or less justified to merge them into one category. In fact, the variations of the intermolecular distance in both strictly bound and quasibound configurations are bracketed within 10–15% of its equilibrium value.[7] Thus the magnitude of the induced dipole moment in a variety of dimeric states can be thought of as being constant and can be determined approximately as an induced dipole moment† taken at equilibrium ground state dimer configuration.

In general the dipole moment induced by one molecular unit due to interaction with another one is strongly coordinate dependent $\mu(r, \Omega)$. Here Ω denotes a set of angular coordinates determining spatial orientation of molecules relative to each other. The average intensity of absorption per one molecular pair S_{ind} can therefore be determined as the squared induced dipole moment μ^2, spacely averaged with the appropriate Boltzmann distribution function:

$$S_{ind} = Q^{-1} \int_{\cdot\Omega\cdot} \int_{\cdot} \int_0^\infty \mu^2 \exp(-U/kT) r^2 \, dr \, d\Omega, \tag{3}$$

$$Q = \int_{\cdot\Omega\cdot} \int_{\cdot} \int_0^\infty \exp(-U/kT) r^2 \, dr \, d\Omega.$$

Here $U(r, \Omega)$ stands for pair intermolecular potential, T is temperature, k is the Boltzmann constant. At large intermolecular separations the potential U is close to zero, so the integral Q is proportional to a gas volume V. The integral in the numerator of (3) does not depend on V and remains limited since the induced dipole moment drops more rapidly than r^{-3} with growing r. Substitution of Eqs. (3) and (2) into Eq. (1) results in the integrated absorption intensity being insensitive to whether the molecules are bound or not. In fact the integrated intensity I equals:

$$I = c \langle \mu^2 \rangle \left(\frac{N}{V} \right)^2. \tag{4}$$

Here c is constant and the angular brackets mean integration over the whole set of spatial variables. Despite the seeming CIA effect being insensitive to the formation of bound and quasibound states the decomposition of integrated intensity or, more generally, CIA band profile into bound, metastable and free contributions is extremely valuable. This is caused by at least two reasons. First, it is common practice, which is, however, by no means justified, to find an average in (4) by using the simplest angular pre-averaged intermolecular potentials and/or by accounting

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†Here and elsewhere under "induced dipole moment" we mean either its permanent constituent, which determines the intensity of far infrared absorption, or the derivative of the induced dipole moment against intramolecular coordinate, which gives rise to absorption in the region of the vibrational fundamental.

for only linear or slightly curvilinear trajectories of colliding molecules. Thus, the contribution from bound + metastable dimeric states is arbitrarily excluded from consideration or at least diminished. Second, to build the CIA band envelope it is highly desirable to discriminate between bound, metastable and free states since each of these types of states can be characterized by its own particular mechanism of formation of individual transitions. This concerns primarily the mechanisms of line broadening. The difference in the spectroscopic properties of bound and quasibound dimers derives mainly from two sources. First, in most cases the transition frequencies of the metastable dimer (or resonance state) cannot be treated by employing the simplest molecular models such as harmonic oscillator or free internal rotor, which are conventionally appropriate in the case of a strictly bound dimer. This has been clearly demonstrated in particular by thorough calculations by Brocks,[8] made for the N_2–Ar molecular dimer. Second, the widths of the individual resonance states are mainly due to life-time broadening. This leads to a very wide distribution of the broadening parameter in accordance with a variety of the excitation levels and the probability for the selected resonance state to be coupled to a dissociation channel.

The induced dipole moment, which appears in the course of elastic collision, can by no means be constant. In this case, the average should be taken over all possible infinitely spread collision trajectories. This means that the averaging procedure cannot be done by spatial integration alone, but must include an integration over a certain domain in the phase space.

Overall CIA intensity (1) can be represented in the following form:

$$I = \frac{N_p}{V}(S_{bm}^{ind} + S_f^{ind}) = I_{bm} + I_f.$$ (5)

Here subscripts bm and f relate to the average over the domains of bound + metastable and free states respectively. The first term in Eq. (5) can be rewritten as follows:

$$I_{bm} = \frac{N_p}{V}S_{bm}^{ind}.$$ (6)

For the sake of simplicity the induced dipole moment for dimers can be taken at the first approximation to be coordinate independent. Consequently $S_{ind} \approx \langle \mu^2 \rangle_{bm} x_{bm}$ and formula (6) is transformed to the following:

$$I_{bm} = \frac{N_p}{V}\langle \mu^2 \rangle_{bm} x_{bm}.$$ (7)

Here x_{bm} is a fraction of bound and metastable states relative to the total number of pair states $x_{bm} = N_{bm}/N_p$ and the average dipole moment $\langle \mu^2 \rangle_{bm}$ is now considered to be constant. It is worth noting that the number of bound and metastable dimers N_{bm} can be expressed via the molar fraction x_2 of dimers in an equilibrium gas, that is $N_{bm} = x_2 \cdot N$, N being the total number of particles. Thus, instead of Eq. (7) the following expression is also valid:

$$I_{bm} = \frac{N}{V}\langle \mu^2 \rangle_{bm} x_2.$$ (8)

It has been shown by Stogryn and Hirschfelder,[9] that bound and metastable dimers are indistinguishable concerning monomer–dimer equilibrium. According to mass-action law $x_2 = Px_1^2/K_p$. Here P stands for total pressure, K_p is equilibrium constant for dimerization reaction, x_1 is the mole fraction of monomers. Making use of the mass-action law together with the ideal gas equation of state $P = (\rho/\bar{m})RT$, a portion of integrated CIA intensity which is related to the bound and metastable states can be represented as follows:

$$I_{bm} = \langle \mu^2 \rangle_{bm} \frac{RT}{K_p}[x_1/\bar{m}]^2\rho^2 \approx \langle \mu^2 \rangle_{bm} \frac{RT}{K_p}\frac{\rho^2}{m_1^2}.$$ (9)

Here R is the gas constant, $\bar{m}$ and m_1 are mean and monomeric molecular masses, ρ is the gas density and the degree of dimerization is supposed to be small. It is seen that the term I_{bm} is proportional to the gas density squared. Equation (9) has been employed in Ref. 10 in interpreting the temperature dependence of CIA intensity in the region of the Fermi dyad of carbon dioxide. The use of this representation can be justified by the results of subdivision of the phase space
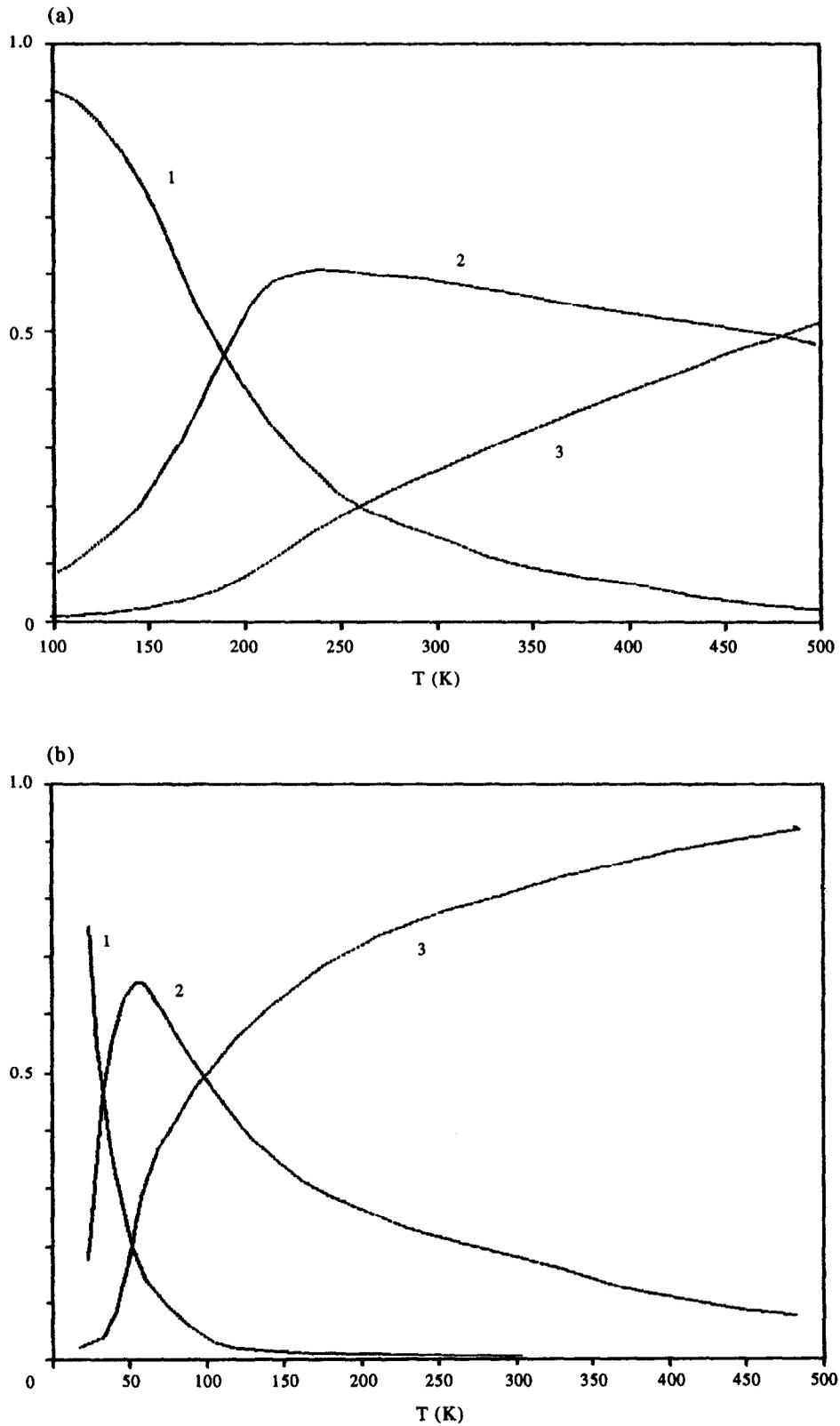
(a)

(b)

Fig. 1. Normalized temperature dependencies of the collision-induced intensity of absorption in (a) carbon dioxide and (b) nitrogen averaged in Ref. 11 over bound (1), metastable (2), and free (3) domains in the phase space.

performed in Ref. 11 to account for the real anisotropic intermolecular potential. Figure 1(a) demonstrates that the contribution to CIA due to inelastic interactions of CO_2 pairs dominates over the free states contribution in the temperature range up to ca. 400 K. Therefore the neglect of purely elastic collisions in Ref. 10 did not give rise to substantial error. This made it possible to interpret successfully in Ref. 10 the temperature dependence of the integrated intensity in the region of the CO_2 Fermi dyad as being exclusively due to bound + metastable dimer formation.

The second term in (5) which relates to free molecular pairs can be represented as:

$$I_f = \frac{N_p}{V} S_f^{ind} = \frac{N^2}{2V} \langle \mu^2 \rangle_f. \tag{10}$$

It has been shown in Ref. 7 that an accurate average of the dipole moment in Eq. (10) can be performed by using the following expression:

$$\langle \mu^2 \rangle_f = C(kT)^{7/2} \int \left[\int_0^\sigma \mu^2(r, \Omega) \exp(-U(r, \Omega)/kT) r^2 \, dr \right.$$

$$\left. - \int_\sigma^\infty \mu^2(r, \Omega) \exp(-G(r, \Omega)/kT) r^2 \, dr \right] d\Omega, \tag{11}$$

where $\int \dots d\Omega \equiv \int_0^\pi \sin \theta_1 \int_0^\pi \sin \theta_2 \int_0^{2\pi} \dots d\psi \, d\theta_2 \, d\theta_1$, C is constant, potential U is equal to zero at $r = \sigma$ (see Fig. 2). In Eq. (11) $G(r, \Omega)$ denotes an auxiliary function first introduced in Ref. 7, which separates the region of free states from rotationally metastable states as it is illustrated in Fig. 2.

Figure 1(b) shows that for the nitrogen pairs the role of free states becomes dominant at temperatures in excess of ca. 120 K. At $T = 75$ K less than 20% of dimers are stable dimers, the rest being in their quasibound states. Therefore while attempting to interpret below the CIA bandshape one has to wait for a substantial contribution of these quasibound or resonance states being embedded under the non-resolved smooth collision-induced profile.

3. COLLISION-INDUCED PROFILE

To build the collision-induced profile it seems reasonable to start from the positions and intensities of individual transitions specific to diatomic molecules. Pure Lorentzians are known to give very poor approximation to actual observed fundamental bandshapes. The role played by a perturbing partner of collision in the line-shape formation may be at least three-fold. First, in purely elastic collisions, which manifest themselves either at relatively large impact parameters or at rather high relative velocities, the rotational movement is expected to be only slightly perturbed. However this may well result in non-optical transitions due to rotational relaxation, that is rotational perturbation may give rise to the line-mixing effect. Second, at the opposite extreme the strictly bound dimers exhibit rather sharp absorption features situated in the vicinity of the monomer Q-branch, since individual rotations of the monomers within a dimer may be thought to be practically blocked. Some evidence of these dimeric absorptions were detected in a number of works, dedicated to infrared (i.r.) studies of different homonuclear diatomics (see, e.g., excellent work by McKellar,[12] on CIA in N_2). Third, and most difficult to interpret is the character of rotational perturbation in metastable dimers. Both the very type of rotational movement and the lifetime of the dimer are strongly affected by a number of factors (position and type of resonance state, level of excitation, closeness to dissociation channel, etc.), so that characteristics of perturbation may vary within wide limits. As a matter of fact one can claim that the real type of movement will be intermediate between hindered rotation in a dimer, which originates from librational movement near its ground state and slightly perturbed rotations in the course of instantaneous impact, which was quoted above for purely elastic collisions. Especially in this latter case one may expect pronounced manifestations of the line-mixing effect. Until an easy and exhaustive way to calculate the positions and widths of resonances is achieved one has to be restricted within the frame of rather crude approximations. As such one can try to take a representation of CIA as being due to a mixture of strictly bound dimers and hindered internally

rotating dimers. This idea has been employed by Henderson and Ewing,[13] in their attempts to interpret the CIA spectrum of O_2-Ar. Despite the success reached in Ref. 13 in describing weak features superimposed onto a collision-induced profile there are reasons (see, e.g., Sec. 2) to suppose, that in the particular case of atom–diatomic or diatomic–diatomic systems the role played by strictly bound dimers is almost negligible and the interacting units are only slightly perturbed. The data presented in Fig. 1(b) (or other results of similar analysis) serve as an indication of the dominant contribution going to nitrogen CIA intensity from purely elastic collisions and resonance states, at least at near room temperatures.

Another possibility to model CIA profile is to assume that it is mainly due to the line-mixing effect. Of course some contribution from the strictly bound states is worth accounting for, especially in the region of the Q-branch. As we shall demonstrate even in complete neglect of the line-mixing within the Q-branch, the overall bandshape can be quite nicely reproduced. As concrete examples of the application of line-mixing formalism we shall consider the CIA profiles of the nitrogen and oxygen fundamentals accordingly in pure gas and in a mixture with argon buffer gas.
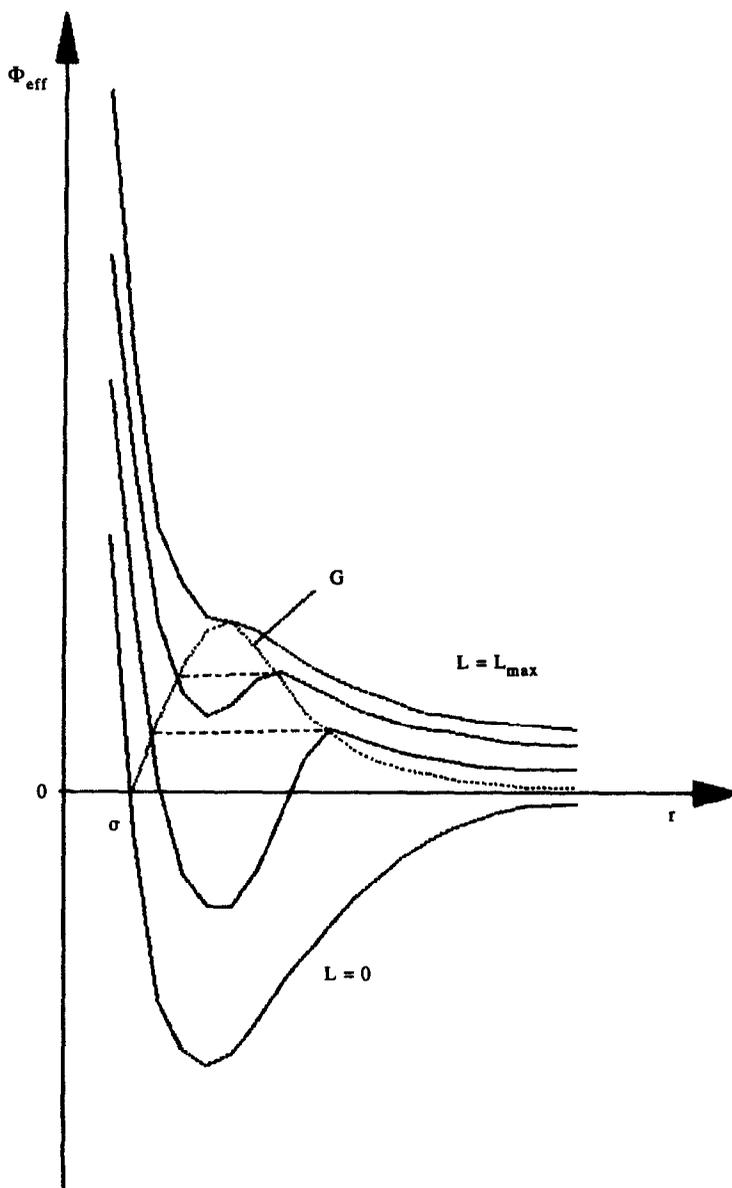

Fig. 2. Qualitative view of the family of the effective potential energy at different end-over-end rotational energies L. Auxiliary function G (see Ref. 7 for rigorous definition) is depicted by (- - -).

3.1. Outline of the line-mixing model

Being homonuclear diatomics, nitrogen and oxygen do not give rise to dipole-permitted i.r. absorption spectra. Since its first detection in Ref. 1 the induced absorption in the region of the N_2 and O_2 monomer vibrational frequencies has been reported in a number of long-path absorption studies, including field atmospheric observations. Accurately measured laboratory spectra seem to follow in their general outline a superposition of strongly broadened and overlapped individual vibro-rotational lines in the O-, Q-, and S-branches, respective to the well-known selection rules for CIA. In a number of cases a structure has been detected on top of the diffuse CIA contour near the band centre region, which can be attributed to van der Waals dimers. For instance such structures were observed in pure nitrogen by Long et al[14] and later by McKellar.[12] According to McKellar[12] weak regular oscillations are superimposed on the generally smooth profile of the CIA nitrogen spectrum taken at $T = 77$ K. An interesting feature of these oscillations, revealed by McKellar, is that the local minima correlate with the positions of the line centres in O- and S-branches, while maxima are found in between the lines. Later Lafferty et al[15] have confirmed this observation and showed that these regular oscillations still remain even at near room temperatures. The nature of oscillations remained obscure up to now. Note that similar oscillations were observed earlier, e.g., in the spectra of O_2–Ar by Henderson and Ewing[13] and were attributed by them to the combination transitions of intramolecular vibration and hindered internal rotations in the corresponding van der Waals complexes. The surprisingly regular character of these oscillations and their being almost independent of the sample temperature made us doubt this attribution. Instead, we are suggesting below an outline of a new mechanism of formation of CIA band shape. Basically this mechanism can account for the line-mixing effect. It seems to be commonplace nowadays to say that line-mixing can play a significant role in the line wings and in the dense Q-branches either in Raman or i.r. spectra. However, no attempts are known to account for line-mixing in constructing the CIA envelopes.

As a basis of our simplified model we have taken the so-called strong collision theory as it is formulated by Bulanin et al.[16] According to this theory the bandshape $\Phi(\omega)$ can be represented as: $\Phi(\omega) = \Phi_L(\omega)\kappa(\omega)$, where $\Phi_L(\omega)$ is the sum of m unmixed Lorentzians with linewidths γ_m and (normalized) linestrengths A_m, $\kappa(\omega)$ is the band-correction function given by:

$$\kappa(\omega) = \frac{S_1(\omega)[1 - S_1(\omega)] - S_2(\omega)}{\{[1 - S_1(\omega)]^2 - S_2(\omega)\}S_3(\omega)},$$
(12)

where

$$S_1(\omega) = \sum_m \frac{A_m}{1 + (\Delta\omega_m^*)^2}$$

$$S_2(\omega) = \left[\sum_m \frac{A_m \Delta\omega_m^*}{1 + (\Delta\omega_m^*)^2}\right]^2$$

$$S_3(\omega) = \sum_m \frac{A_m(1 - A_m)}{(1 - A_m)^2 + (\Delta\omega_m^*)^2}.$$

Here $\Delta\omega_m^* = \tau(\omega - \omega_m)$, τ being the rotational relaxation time. Within the frame of the strong collision model the semiwidths of Lorentzians, which are equal to diagonal elements of the relaxation operator Γ, can be expressed as

$$\gamma_m = \Gamma_{mm} = \tau(1 - A_m),$$
(13)

while non-diagonal elements are equal to

$$\Gamma_{mm'} = \tau^{-1}\sqrt{A_m A_{m'}}.$$

The model of Bulanin et al[16] was taken by us with just three modifications. First, it was supposed that different mechanisms are able to contribute to the broadening of the individual

vibro-rotational lines. Therefore, true Lorentz linewidths may differ from Eq. (13). Second, the relaxation time is not considered necessarily as being due to rotational relaxation by collisions. The true nature of the relaxation mechanism is out of the scope of this work. Third, we neglect completely the interbranch mixing and restrict ourselves to account for the line-mixing only in O- and S-branches. This is in line with the conclusion drawn in Ref. 16, that interbranch mixing relates to a less probable process than intrabranch mixing. To compensate the neglect of line-mixing in the Q-branch we have supposed that Lorentz linewidths in the Q-branch may differ from those in the O- and S-branches. Finally, three adjustable parameters are imbedded in the present model. They are Lorentz lineshapes semiwidth γ_1 for the lines in the Q-branch, semiwidth γ_2 for the lines in the O- and S-branches and relaxation time τ. These parameters were found in the course of non-linear least-square fitting of experimental spectra. The pure nitrogen spectra taken by McKellar[12] at 77 K and by Lafferty et al[15] at six temperatures in the vicinity of room temperature have been employed. The oxygen spectrum taken by Henderson and Ewing[13] was not available to us in digital form, so the points were taken by hand from the publication drawing. Of course the accuracy of this representation of the oxygen spectrum is insufficient and the reconstruction of its profile is only illustrative.

To calculate the positions and linestrengths of the individual rotovibrational transitions the following expressions were used:

$$\omega_m = E_f - E_i$$

$$E_i = B_0 j''(j'' + 1) - D_0[j''(j'' + 1)]^2$$

$$E_f = B_1 j'(j' + 1) - D_1[j'(j' + 1)]^2$$

$$A_m = C(j'')\exp\left(-\frac{E_i(j'')}{kT}\right).$$

Here

$$C(j'') = \begin{cases} \dfrac{3j''(j'' - 1)}{2(2j'' - 1)} & \text{—}O\text{-branch} \\[3mm] \dfrac{j''(j'' + 1)}{(2j'' + 1)(2j'' - 1)(2j'' + 3)} & \text{—}Q\text{-branch} \\[3mm] \dfrac{2(j'' + 1)(j'' + 2)}{2(j'' + 3)} & \text{—}S\text{-branch.} \end{cases}$$

Rotational constants for nitrogen were taken from Reuter et al:[17]

$\omega_0 = 2329.91239\,\text{cm}^{-1}$
$B_0 = 1.989622\,\text{cm}^{-1}$
$B_1 = 1.9722523\,\text{cm}^{-1}$
$D_0 = 5.763 \cdot 10^{-6}\,\text{cm}^{-1}$
$D_1 = D_0.$

Intensity alternation due to nuclear spin statistics has been accounted for. The following constants were adopted for the oxygen molecule from Refs. 18 and 19:

$\omega_0 = 1556.384\,\text{cm}^{-1}$
$B_0 = 1.437682\,\text{cm}^{-1}$
$B_1 = 1.421884\,\text{cm}^{-1}$
$D_0 = 4.852 \cdot 10^{-6}\,\text{cm}^{-1}$
$D_1 = -4.864 \cdot 10^{-6}\,\text{cm}^{-1}.$

For the nitrogen molecule the positions of lines calculated with the above constants fit the data given in Ref. 17 well. However, the linestrength distribution slightly deviates from that calculated in Ref. 17 for 296 K. For the fitting of the absorption coefficient, normalized to its maximum value, the following formula has been used:

$$K_m(\omega) = K_{max}^{-1}\omega[1 - \exp(-\hbar\omega/kT)] \sum_m^N \frac{A_m\gamma_m}{\gamma_m^2 + \Delta\omega_m^2} \kappa(\omega) \frac{2}{1 + \exp(-\hbar\omega/kT)}.$$

The last term in this expression accounts for the detailed balance principle, $\kappa(\omega)$ is given by Eq. (12) for O- and S-branches and equals unity for the Q-branch. The total number of lines N taken into consideration equals 90 for nitrogen and 60 for oxygen.

3.2. Results and discussion

All the spectra (at seven different temperatures for nitrogen and at $T = 93$ K for oxygen) were successfully fitted with approximately the same accuracy. In all cases the average relative standard deviation

$$\sigma = \sqrt{\frac{1}{M} \sum_1^M [K_{exp}(\omega) - K_{calc}(\omega)]^2}$$

was about 0.02–0.03. Note that the nitrogen experimental spectra were represented by $M = 800$ equidistant points for $T = 77$ K and $M = 1700$ points for the rest of the spectra. In the case of oxygen the number of points equals $M = 186$. Figures 3–5 demonstrate that the overall bandshapes are quite nicely reproduced, albeit no specific sublorentz lineshapes in the wings were supposed. This is due to the general feature of line-mixing effect, which tends to decrease the intensity in the
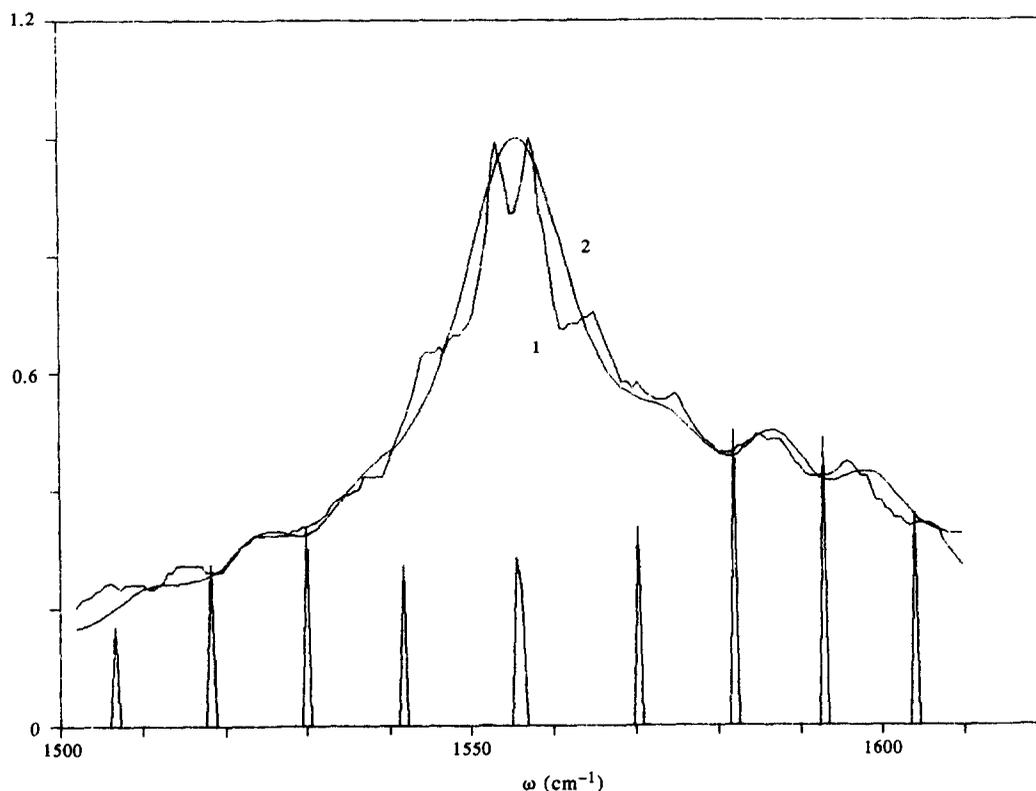

Fig. 3. Normalized collision-induced profiles for the oxygen fundamental band in a mixture of O_2 and Ar. 1—Experimental spectrum from Henderson and Ewing,[13] 2—simulated spectrum. Stick spectrum is shown in the bottom part of the figure as used in the calculations for $T = 93$ K.
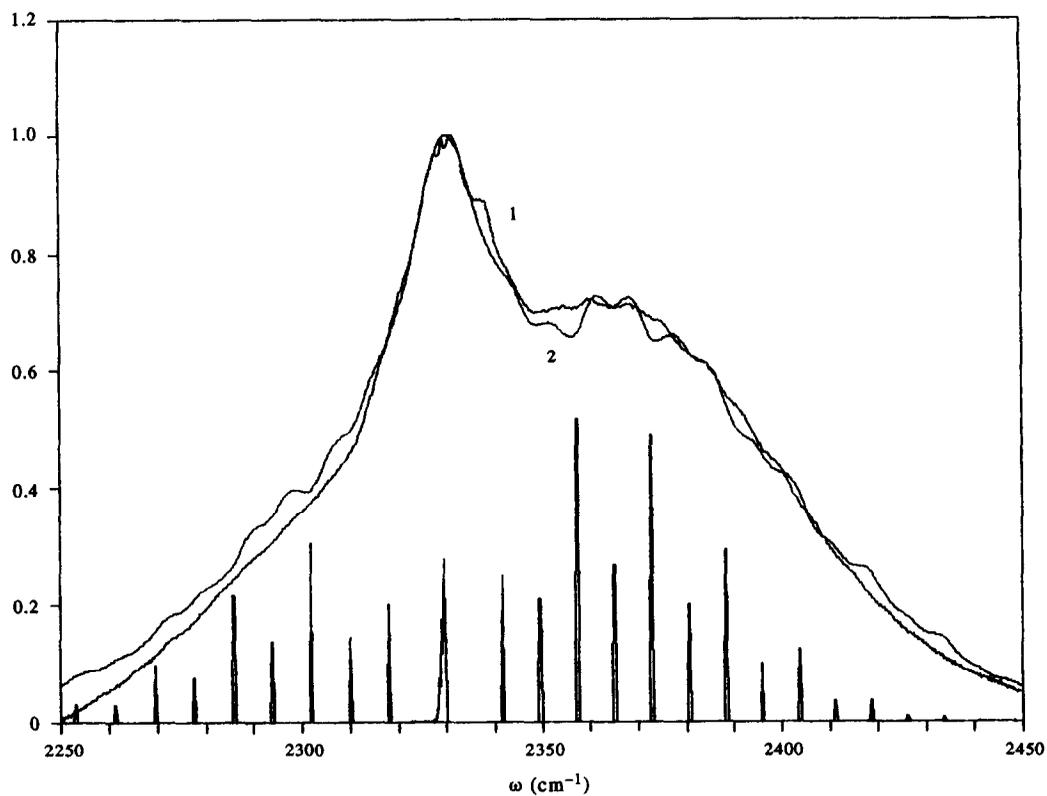
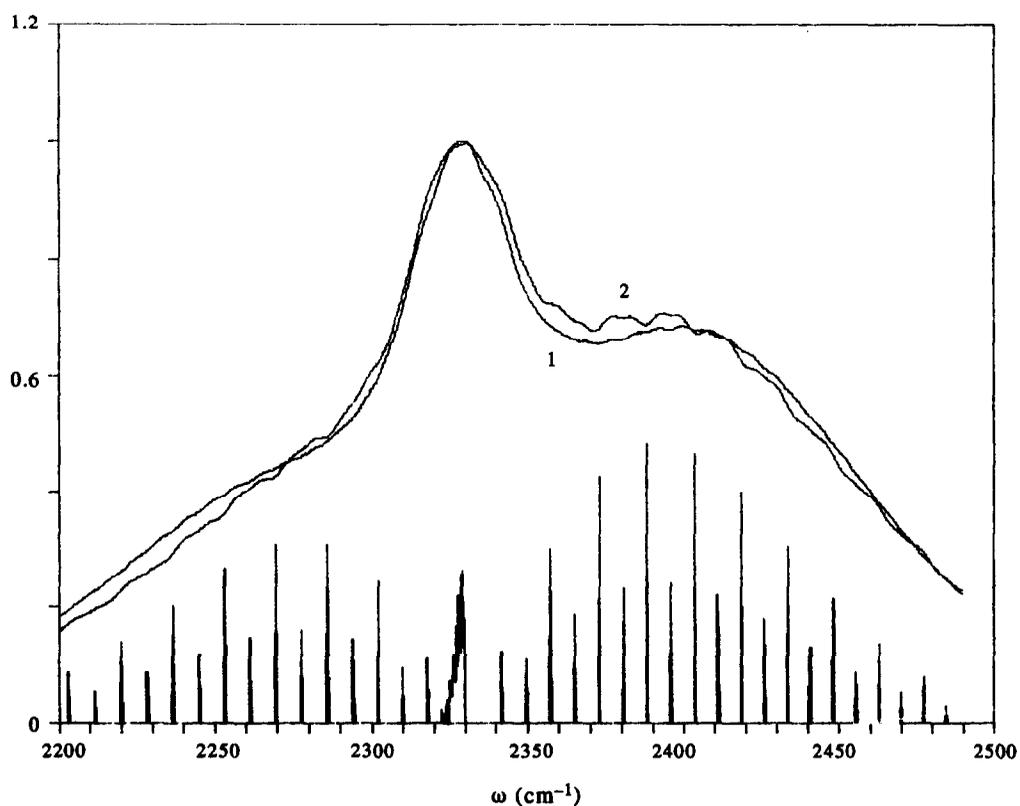Fig. 4. As in Fig. 3 for nitrogen at $T = 77$ K. Experimental spectrum (1) is taken from McKellar.[12]

Fig. 5. As in Fig. 3 for nitrogen at $T = 296.26$ K. Experimental spectrum (1) is taken from Lafferty et al.[15]
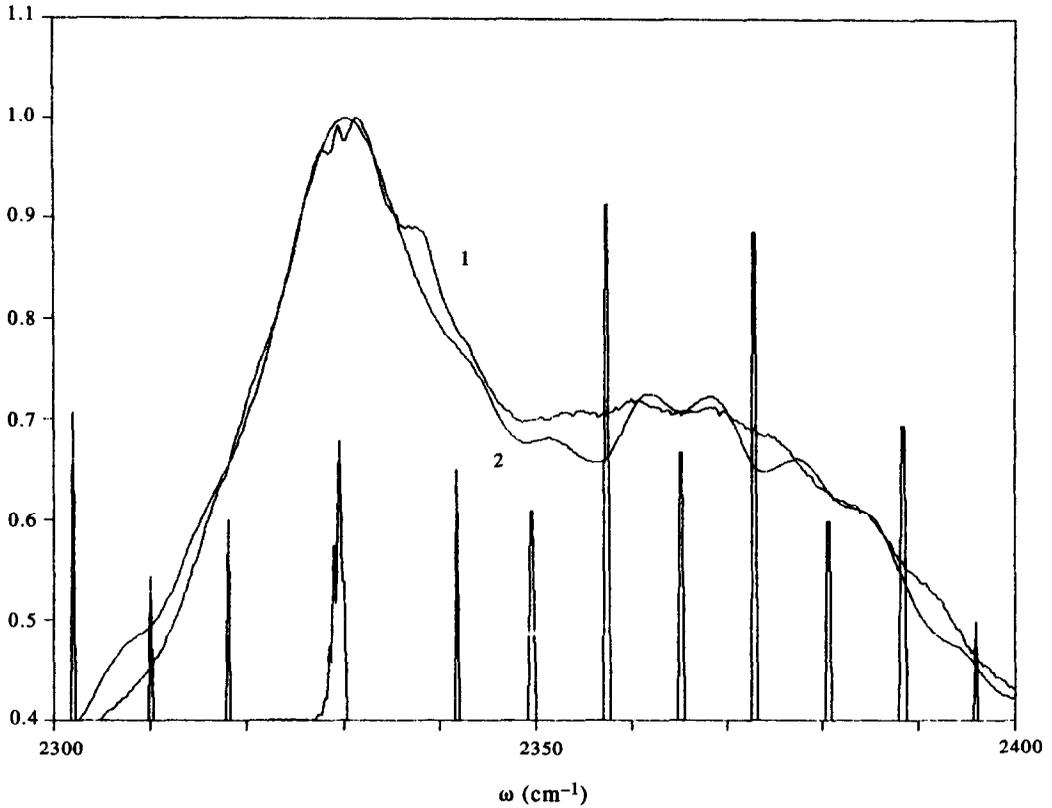
Fig. 6. A portion of spectra shown in Fig. 4. Note the correlation of the minima in the measured (1) and calculated (2) spectra with the positions of sticks.
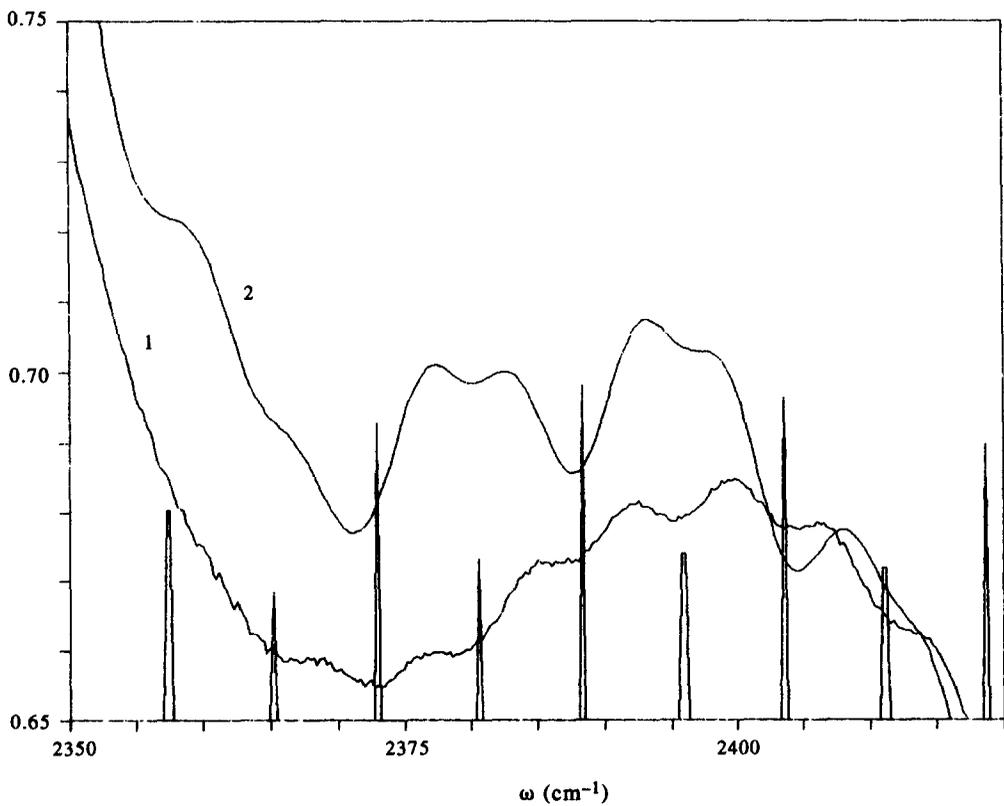

Fig. 7. A portion of spectra shown in Fig. 5.

band-wings at the expense of increase in the region of the strongest lines. Moreover, in all cases weak regular oscillations are clearly seen in the calculated spectra. Their amplitudes are somewhat in excess of what is observed in experimental spectra, but the sequence of maxima and minima coincide reasonably well with experimental data. Note that the results of application of our line-mixing model to O_2–Ar system demonstrate reproducibility of the bandshape notwithstanding low quality of the available experimental spectral curve. Good correspondence between the calculated and measured ripples in the nitrogen spectra and their relation to the stick spectrum is illustrated by Figs. 6 and 7.

Our concluding remark concerns the temperature dependence of the parameters found in the course of spectral fitting. Figures 8(a) and 8(b) accumulate these dependencies. Three aspects here deserve to be mentioned. First, temperature dependence of the broadening in the Q-branch $\gamma_1(T)$ is strictly linear. Second, temperature dependencies of $\gamma_2(T)$ and $\tau(T)$ for the near-room temperature spectra are not pronounced. However this may be due to ill determined solution of the inverse optimization procedure. Third, temperature dependence of the relaxation time $\tau(T)$ qualitatively follows that, known for the collisional rotational relaxation time τ_{rot}, given, e.g., by Parker's formula.[20] Note that the scattering of the known experimental data on τ_{rot} is so significant, that even the function $\tau(T)$, depicted in Fig. 8(b) may well be taken as true dependence of $\tau_{rot}(T)$.

4. CONCLUSIONS

The main conclusion of the present work consists in making evident the importance of the metastable or resonance dimeric states for collision-induced bandshape modelling. It has been shown that the neglect of anisotropy of intermolecular interaction results in underestimation of the role played by metastable state formation. The phenomenon of collision-induced absorption reduces in some cases to purely dimeric absorption, provided metastable states are included in dimeric states. To model the overall CIA bandshape and to reveal the nature of weak regular ripples
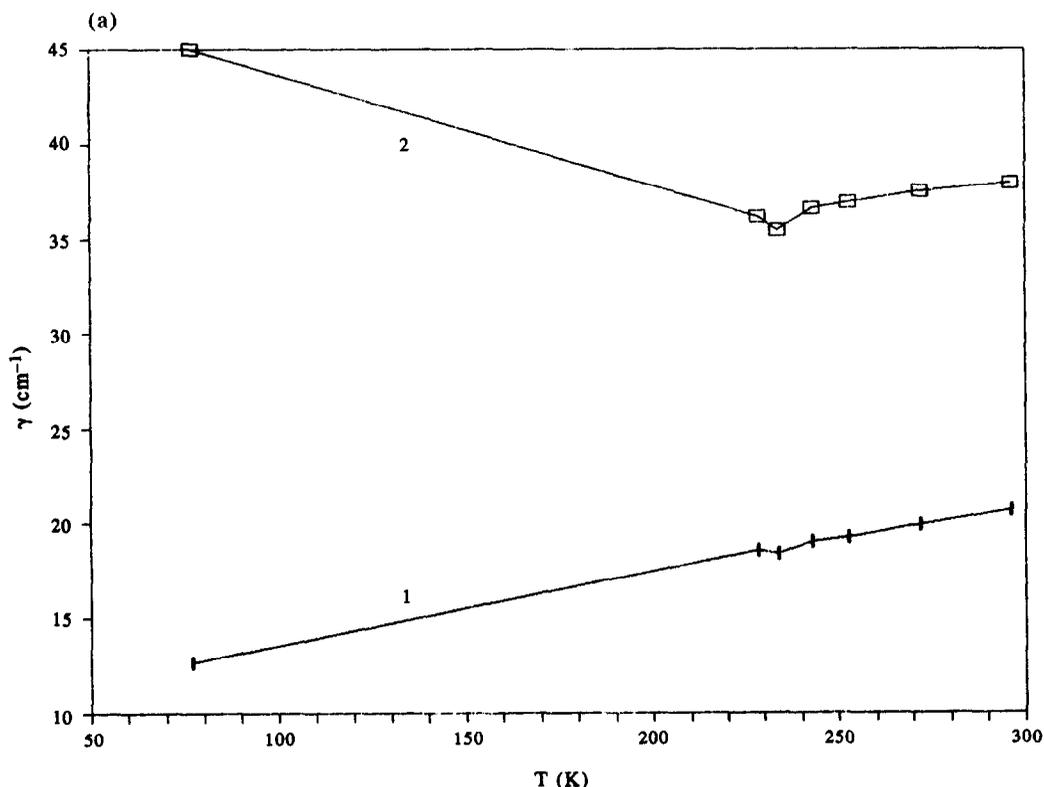

Fig. 8. (a) Temperature dependencies of linewidth $\gamma_1(T)$ in the Q-branch (1) and $\gamma_2(T)$ in O- and S-branches (2), taken from the spectral fitting of the nitrogen fundamental bandshape at seven different temperatures.
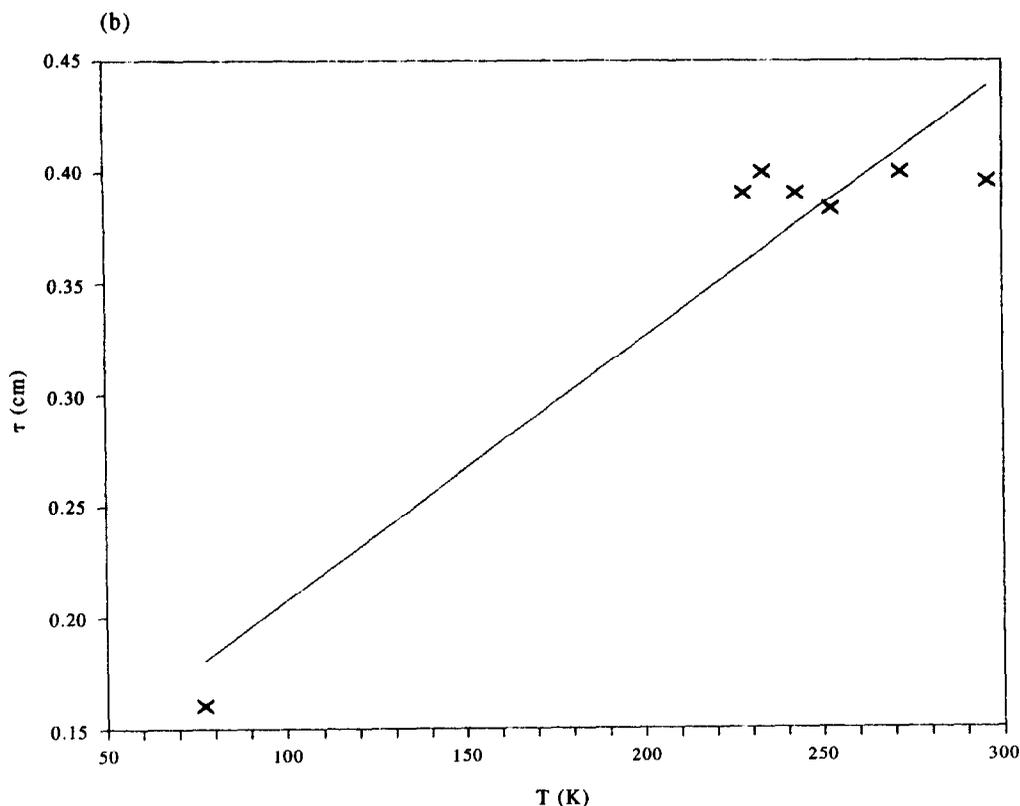
(b)

Fig. 8. (b) Relaxation time $\tau(T)$ as a function of temperature derived in the course of the same spectral fitting of the nitrogen fundamental bandshape as linewidths depicted in Fig. 8(a).

superimposed onto CIA diffuse background one has to account for rotational perturbation of free or loosely bound monomers. This can be done either by considering hindered internal rotation within a dimer or better by applying the line-mixing formalism. We have demonstrated that collision-induced bandshapes in pure nitrogen and in a mixture of O_2 + Ar may be reasonably well reproduced even in their tiny details by accounting for the line-mixing effect. Further development of the suggested approach and its extension to other colliding partners seems very promising and fruitful.

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