Band shape transformation in spectra of spherical top molecules: manifestation of Coriolis interaction

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IR absorption spectra of gaseous CF_4 mixed with Ar and He in the ν_4 band region are studied at the buffer gas pressures from 0.5 to 300 atm. The line mixing effect seems to influence essentially the band shape. The pressure induced broadening of the Q-branch is essentially less than that of individual rotation-vibration lines and depends on a buffer gas. The broadening coefficients for J-multiplex are determined. To make band shape calculations, we propose a model relaxation matrix taken as a linear combination of matrices for weak and strong collision limit cases. This model with one fitting parameter characterizing the intensity of collisions provides an appropriate description of the obtained data set.

Transformation of rotation-vibration bands in molecular spectra at gas pressure variation cannot be reduced to merely broadening of component lines. In some cases at line overlapping, nonadditivity effects related to relaxation processes in absorbing molecules arise; these effects are commonly called line mixing. This phenomenon is studied most thoroughly for diatomic and linear molecules, but some recent publications have been devoted to more complicated systems, such as, for example, tetrahedral molecules.[1–4]

It was shown in these papers that three stages can be isolated in the transformations of rotation-vibration bands of such molecules. At the first stage, line mixing essentially affects the shape of J-multiplexes split due to tetrahedral distortions. In methane spectra, this effect manifests itself at the pressure ranging from about 0.5 to 5 atm, and the deviation of the observed absorption coefficients from the mere sum of Lorentz lines in this case can be more than twice.[4]

At a higher pressure, line mixing is observed between different J-multiplexes inside rotation-vibration branches; this effect becomes noticeable, first of all, for the Q-branch. In the $\tilde{N}\acute{I}_4$ spectrum, this occurs at a pressure of 10 atm. At the further increase of the pressure, the interaction between branches begins to manifest itself, thus leading to transformation of the band as a whole. For methane this occurs only at transformation into the condensed state.

In this paper, we present the tentative results on shape transformation in rotation-vibration bands of tetrafluormethane (CF_4) at the increasing pressure of buffer gases (He, Ar). Since the rotational constant of this molecule is an order of magnitude smaller than that of the CH_4 molecule, all the stages occur at the far lower pressure.

The spectra of gas mixtures of CF_4 with helium and argon were obtained at the pressure from a few fractions of atm up to 300 atm. The low-pressure spectra of sample mixtures were recorded with a Bruker HR-120 FTIR at the Renn-1 University (France) with the resolution of $0.02\ cm^{-1}$ in ordinary gas cells. The high-pressure spectra were recorded with a Bruker IFS-28 FTIR at St. Petersburg University (Russia) with the resolution of $0.6\ cm^{-1}$. Gas samples were placed in specially manufactured high-pressure cells with fluorite or KRS-5 windows.

Low pressure

For the CF_4 molecule at the pressure of about 1 atm, the structure of J-multiplexes is almost hidden, and significant line overlap is observed. At such pressure, the second stage of the shape transformation begins, namely, blurring of the whole rotational branch accompanied by mixing of lines belonging to different multiplexes.

The CF_4 molecule has only two F_2-type bands active in the IR. Because of strongly different Coriolis constants ($\zeta_3 = 0.86$ and $\zeta_4 = -0.36$) the ν_3 and ν_4 rotation-vibration bands have absolutely different profiles. The rotational structure of the ν_3 band is very dense, and the ν_4 band is much wider. Besides, the P-branch of the ν_3 band is severely distorted by hot bands. Therefore, our investigations were mainly performed for the ν_4 band. Besides, we observed the E-type forbidden ν_2 band near ν_4. The similar $\nu_1 + \nu_2$ (E) band was also observed near ν_3. Both these bands are induced by the Coriolis interaction.

At the pressure growth and line overlap, the profile calculated in the additive approximation usually differs most strongly from the experimental one for the Q-branch. Indeed, we observed this effect already at the atmospheric pressure (Fig. 1).

At the increasing pressure, the width of the Q-branch increases much more slowly than individual

rotation-vibration lines do: the corresponding broadening coefficients for the Q-branch are an order of magnitude smaller than those for lines. Besides, the broadening coefficients of the Q-branch for mixtures with helium and argon differ more than twice (Fig. 2), while for individual lines these values are usually close. These regularities in transformation of the branch shape show that this shape is essentially determined by line mixing.
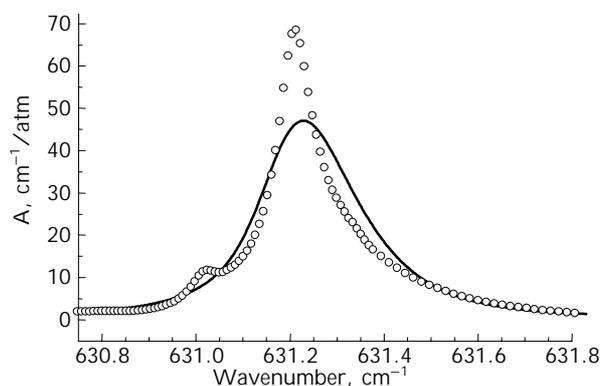
Fig. 1. Spectrum of the CF_4 + He mixture at the pressure of 1 atm in the Q-branch of the ν_4 band: experimental data (dots), the curve was calculated as a sum of Lorentz lines neglecting hot transitions.
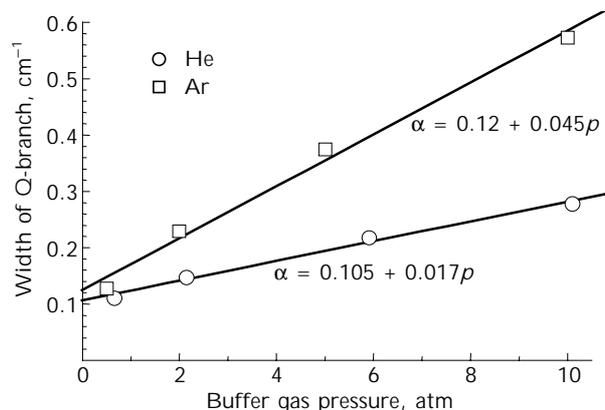
Fig. 2. Width of the Q-branch of the CF_4 ν_4 band as a function of the buffer gas pressure.

It is interesting to note that the broadening coefficients obtained for the Q-branch of the CF_4 ν_4 band (0.017 cm^{-1}/atm for He and 0.045 cm^{-1}/atm for Ar) almost coincide with the coefficients for the Q-branches of the CO_2 bands for the corresponding buffer gases (0.0154 cm^{-1}/atm for He and 0.043 cm^{-1}/atm for Ar) that were measured earlier.[5]

The broadening coefficients for the Q-branches of the E-type bands induced by the Coriolis interaction prove to be smaller than those for the allowed bands of the F_2 type. The coefficient is especially small for the case of He as a buffer gas and the $\nu_1 + \nu_2$ band — only 0.008 cm^{-1}/atm, and thanks to that small value, the branch structure of this band keeps unchanged even at 300 atm. For the mixture

with argon this coefficient is larger (0.03 cm^{-1}), but it still does not exceed the corresponding value for the allowed bands. Broadening of the Q-branch of the ν_2 band for pure CF_4 (0.08 cm^{-1}/atm) turns out to be markedly smaller than that for the Q-branches of pure CO_2 (0.12 cm^{-1}/atm). In our opinion, this result can be connected with differences in the structure of the P- and R-branches of the allowed bands as compared to the bands induced by the Coriolis interaction.

Under conditions of completely blurred rotational structure of the Q-branch, relaxation processes connected with spectral exchange inside this branch already have no marked effect on its width. The width in this case is determined by mixing of lines belonging to this branch with lines of neighboring branches. At the same time, the intensity distribution in the rotation-vibration structure of the P- and R-branches is different for the allowed bands and the bands induced by the Coriolis interaction. In the first case, the line intensity is proportional to $J^2 \exp[-E(J)/kT]$, while in the second case it is determined by the factor $J^4 \exp[-E(J)/kT]$. This means that the strongest lines of the P- and R-branches of the induced band correspond to high quantum numbers, while the lines with low J become effectively weaker. Just this difference likely determines the difference in the broadening coefficients for the Q-branches of these bands.

At the pressure of 1 atm, the structure of J-multiplexes in CF_4 rotation-vibration bands is blurred, and at sufficient separation between them, as in the ν_4 band, they are broadened as individual lines. However, their transformation is similar to that occurring for the Q-branch, that is, at extrapolation to zero pressure, a line has a residual width caused by tetrahedral splitting. Having described the pressure p dependence of the total width of lines α by the function

$$\alpha(p) = \alpha_0 + \gamma p, \qquad (1)$$

we estimated the broadening coefficients γ. The values of γ obtained for the mixtures of CF_4 with He and Ar are depicted in Fig. 3. It is interesting to note that the obtained broadening coefficients for the multiplexes are smaller than those for individual lines, and they essentially depend on the quantum number J even for the mixture with helium, while individual lines usually do not show such a dependence of the broadening coefficient on J. The broadening coefficients determined were used in further calculations of the ν_4 band shape.

Line positions needed for our calculations were borrowed from Ref. 6. We found that theoretical branch intensity ratio for a rigid rotor $I(P + R)/I(Q) = 2$ did not correspond to the experimental value of 2.23 determined by us. It was just this value that we used in our calculations of line intensities. Inside a branch, the line intensity distribution was calculated by equations for a rigid rotor with a modernization for the determined

empirical Hermann–Wallis factor $F(J) = (1 + cJ)^2$ at the parameter $\bar{n} = 0.002$.
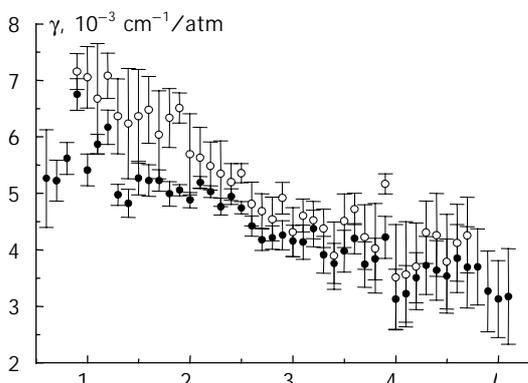
Fig. 3. Broadening coefficients for multiplexes of the ν_4 band in the cases of CF_4 mixture with helium (î) and argon (•).

Band shape at high pressure

The most commonly used method for calculating the shape of rotation-vibration bands formed by overlapped lines employs the well-known equation

$$A(\omega) = \frac{4\pi^2(\omega + \omega_0)}{3\hbar c}\left[1 - \exp\left(-\frac{\hbar(\omega + \omega_0)}{kT}\right)\right]\Phi(\omega) , \quad (2)$$

where ω is the frequency detuning measured from the band origin ω_0; $\Phi(\omega)$ is the spectral function that contains the main information about the band shape. The use of the Liouville space formalism allows the spectral function to be written as:

$$\Phi(\omega) = \frac{1}{\pi} \, \mathrm{Re} \, \langle\langle M| \frac{1}{i(\omega - L_0) + \Gamma}|M\rangle\rangle, \quad (3)$$

where $|M\rangle\rangle$ is the dipole moment operator, which is a vector in this space, and the operator L_0 forms a diagonal matrix of molecular rotational frequencies measured from the band origin. The operator Γ forms the relaxation matrix of rotational transitions. Diagonal elements of the real part of this matrix determine linewidths, while the off-diagonal ones are responsible for the line mixing effects. The imaginary part of this matrix is related to line shifts and can be neglected here.

Determination of the rotational relaxation matrix is the main stage in calculation of spectral profile. In principle, it can be calculated by the *ab initio* methods, but such calculations are extremely cumbersome and can be completed only for some particular cases. Therefore, various empirical methods have been developed for this purpose.

The simplest model of the relaxation matrix employs the approximation of strong collisions, in which for complete relaxation to occur it is sufficient for all molecules to undergo, on the average, one collision. In this model, it is possible to write the elements of the relaxation matrix and invert the matrix in Eq. (3) analytically.

The model of strong collisions gives good results for pure gases,[7] but it is not the case for the ν_4 band of CF_4 in the mixture with argon. The width of the Q-branch in the calculated spectrum proves to be much larger than in the experimental spectrum (Fig. 4).
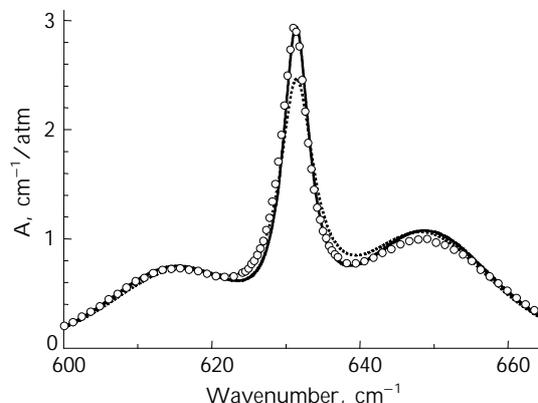
Fig. 4. Spectrum of CF_4 in the mixture with argon at 100 atm, ν_4 band: experiment (dots), calculation with the matrix $\Gamma = 0.7\Gamma^{strong} + 0.3\Gamma^{weak}$ (solid curve), and the model of strong collisions (dashed curve).

The situation for the mixtures with helium is even worse. We explain this by the fact that actual collisions for these pairs cannot be considered strong. To correct the situation, for profile calculations we used the matrix composed as a linear combination of the strong collision matrix (Γ^{strong}) and the weak collision matrix (Γ^{weak}). The latter assumes that every line interacts with only two closest neighbors. Thus formed new matrix has the form

$$\Gamma = C \, \Gamma^{strong} + (1 - C) \, \Gamma^{weak}. \quad (4)$$

This model can be called the model of variable strength of collisions. Note that the matrix similar to Γ^{weak} proposed by us was earlier introduced by Rosenkranz[8] for calculation of oxygen spectrum in the submillimeter region. However, he used the rule of sum for matrix elements that is applicable only to isotropic Raman scattering, but inapplicable to absorption. In our model we calculated the matrix Γ^{weak} using the symmetry conditions and the rule of sum for lines of every branch:

$$\Gamma_{J,J}^{weak} = -\frac{1}{\sqrt{A_J}} \sum_{J'=J\pm1} \sqrt{A_{J'}} \, \Gamma_{J,J'}^{weak}, \quad (5)$$

where A_J is the line intensity. The relaxation matrix determined in such a way does not allow us to invert Eq. (3) analytically, but numerical inversion is not computationally expensive, as the matrix Γ^{weak} is very simple.

The model proposed with only one coefficient C that is determined from fitting to one of experimental spectra for each mixture provides for a good description of the band shape (Figs. 4 and 5), which keeps for the whole dataset. The determined weighting coefficients

of the strong collision matrix $C = 0.7$ for the mixture with argon and $C = 0.08$ for the mixture with helium show that even for the mixture with argon collisions cannot be considered strong, and collisions with helium are close to weak.
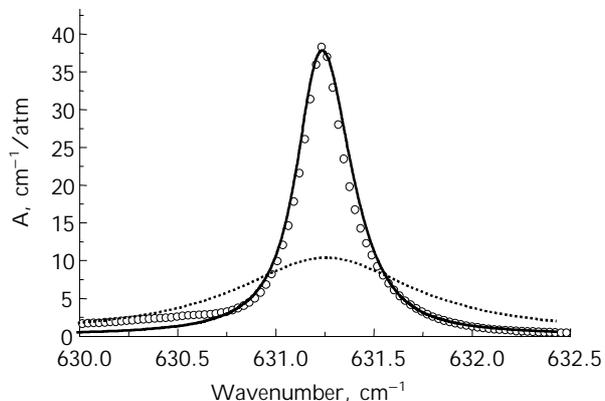
Fig. 5. Spectrum of CF_4 in helium at 10 atm in the region of the Q-branch of the ν_4 band: experiment (dots), sum of Lorentz lines (dashed curve), and calculation with the matrix $\mathbf{\Gamma} = 0.08\mathbf{\Gamma}^{strong} + 0.92\mathbf{\Gamma}^{weak}$ (solid curve).

The results of this work are indicative of the significant role of line mixing in the formation of band shapes of CF_4 in gas mixtures and the high promises of the model proposed for shape calculations.

Acknowledgments

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