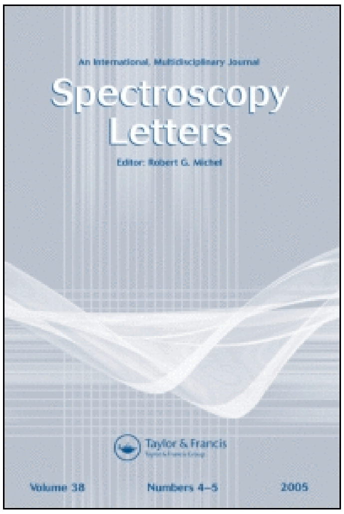

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Effect of Foreign Gases on IR Absorption Bands of Polyatomic Molecules

N. A. Borisevich[a]; G. A. Zalesskaya[a]; V. A. Lastochkina[a]; T. Shukurov[a]
[a] Institute of Physics, BSSR Academy of Sciences, Minsk, USSR

To cite this Article Borisevich, N. A. , Zalesskaya, G. A. , Lastochkina, V. A. and Shukurov, T.(1982) 'Effect of Foreign Gases on IR Absorption Bands of Polyatomic Molecules', Spectroscopy Letters, 15: 12, 991 — 1008

To link to this Article: DOI: 10.1080/00387018208068034

URL: http://dx.doi.org/10.1080/00387018208068034

SPECTROSCOPY LETTERS, 15(12), 991-1008 (1982)

EFFECT OF FOREIGN GASES ON IR ABSORPTION BANDS OF POLYATOMIC MOLECULES

Key Words: Infrared, Absorption bandshape, High pressure, Gas mixture, Dipole correlation function, J-diffusion model

N.A. Borisevich, G.A. Zalesskaya
V.A. Lastochkina, T. Shukurov

Institute of Physics, BSSR Academy of Sciences
Minsk, USSR

ABSTRACT

The effect of foreign gases (He, Ar, N_2 and CO_2) on IR vapour absorption bands corresponding to the vibrations of different symmetry is studied for some symmetric-and asymmetric-top molecules (chloroform, bromoform, trichlorethylene, chlorbenzene, naphthalene). It is shown that rotational P-, Q- and R-branches collapse and a single structureless bandshape appears when foreign gases are added at no more than 75 atm pressure of CO_2 or 175 atm of N_2. A conclusion is made that the contour variations in high pressure gas mixtures are satisfactorily interpreted by the J-diffusion model, i.e. these are related to an increase of hindering of free rotation at binary collisions that change both the direction and magnitude of the angular momentum of molecules. Difficulties appear in the J-diffusion model calculations of the whole absorption bandshape with one angular momentum correlation time, τ_J, as with increasing pressure the central part and the wings of absorption bands may broaden in different ways. It is shown that differences in a structureless absorption band contour for gas mixtures and solutions are attributed not only to the different nature of the rotational motion of molecules in these two cases but also to the small contribution of the vibrational relaxation to the contours of gas mixture bands.

INTRODUCTION

The problems arisen in the last decades in modern photophysics of polyatomic molecules, laser chemistry and biology have initiated further active investigations of molecular relaxation processes by means of the kinetic and traditional spectroscopy methods. The molecular motion models suggested to interpret relaxation processes in dense gases [1,2] are based on the following assumptions. A molecule undergoes only instantaneous collisions. The rotation of molecules between collisions is free. The collisions change the direction of the rotational angular momentum vector of a molecule. Its magnitude either remains unchanged (M-diffusion model) or changes following the Maxwell distribution (J-diffusion model). At present the J- and M-diffusion models are being critisized[3] since even the first attempts to analyze the molecular rotation using the vibrational-rotational contours of liquids and gases involved difficulties in interpreting some experimental results. It is most reasonable to use these models of molecular motion for dense gases where, unlike condensed media, the molecular interactions are more similar to the instantaneous binary collision-induced disturbance of free rotation.

From the experimental results for vibrational absorption bands of small molecules, it was assumed for a long time that the contribution of vibrational relaxation to the formation of vibrational-rotational contours of gases and vapours is small[4,5]. This was included by the models[4,5] to analyze vibrational contours with the lifetime of the vibrational level assumed to be infinitely high. New experimental data have excited the discussion of the vibrational relaxation contribution to vapour bandshapes of polyatomic molecules[7,8].

In the present work, changes of IR absorption bands at increasing foreign gas pressures have been studied for some symmetric- and asymmetric-top molecules with different inertia moments and, hence, with different rotation speeds. The change due to increasing pressure are compared with the predictions of the J- and M-diffusion models to estimate the collision contributions to the contour transformation.

EXPERIMENTAL RESULTS

Spectra were recorded on the Perkin-Elmer spectrometer-180, with a spectral slit width no more than 0.5 cm^{-1}. Measurements were made in a special heated high-pressure gas cell[9]. He, Ar, N_2 and CO_2 at pressures up to 150 atm served as foreign gases.

Isolated absorption bands corresponding to vibrations with differently directed transition dipole moments along the molecular axes were chosen for study. The chosen bandshapes were not distorted due to overlapping with other fundamental, combination or overtone absorption bands. But additional low-frequency absorption due to "hot" transitions appeared within the contours of the majority of bands. A thorough analysis of the investigated absorption bands of chlorbenzene, chloroform and bromoform[10,12] did not exhibit distortion of the central part of the contour by "hot" transitions. For the naphthalene absorption band (ν_{max}= 1011.5 cm^{-1}) at T=423 K the high-frequency half of the contour was analyzed to eliminate the distorting effect of "hot" transitions.

Figure 1 illustrates area-normalized contours of the vapour absorption bands of several substances at different pressures of N_2. All bandshapes are characterized by the following drastic changes observed at increasing pressure of foreign gases.

(1) At increasing pressure of N_2, the structure of rotational branches undergoes substantial changes. This includes changes in the maximum-intensity ratios, Q--branch broadening and R- and P-branch smoothing of parallel and quasi-parallel bands. As a result, the rotational branches overlap still more since pressure increases and form a single contour for the majority of the bands at N_2 pressure of 150 atm.

(2) The perpendicular bands of symmetric-top molecules undergo much smaller changes than the parallel ones[11,13] when foreign gases are added. At initial pressure increase, as is seen from the chloroform absorption band (Fig. 1) the traces of rotational branches, if these occur at all, are smoothed, the band widths being almost invariable. A subsequent pressure increase may inconsiderably narrow the band (2 cm^{-1}). Similar changes are observed in the B-type bands of asymmetric-top molecules. In the test pressure range, the dip vanishes at the centre of the trichlorethylene band, and the contour with a single maximum is formed.

(3) The disturbing effect of He and Ar in many cases proves to be weak. The addition of CO_2 and N_2 in equal proportion yields similar but stronger changes of vibrational-rotational contours. Thus, CO_2 of 75 atm pressure has always produced stronger contour transforma-

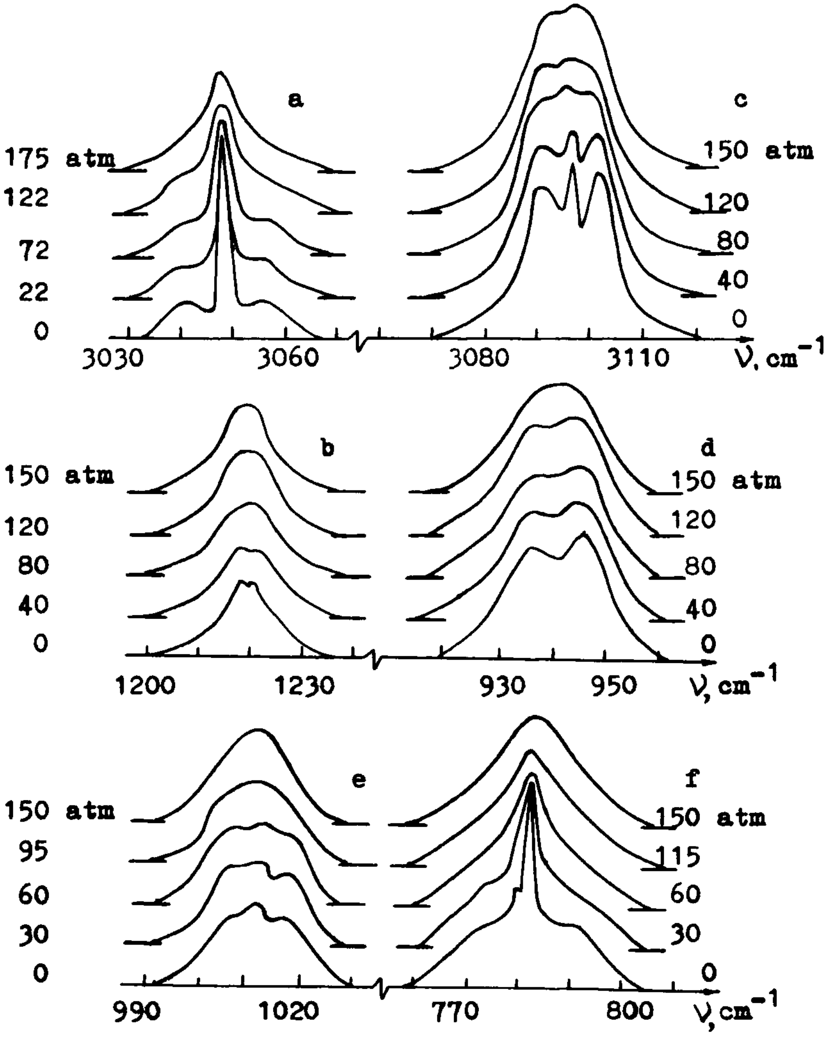

Fig. 1. IR absorption bands of vapours mixed with N_2 (area-normalized): a, bromoform at T=353 K; b, chloroform at T=298 K; c,d, trichlorethylene at T=298 K; e, naphthalene at T=423 K; f, naphthalene at T=348 K.

tion, as compared to maximum N_2 pressure amounting to 175 atm. It should be noted that considerable pressures of N_2, Ar and He in all cases have improved the contour symmetry. But several absorption bands of chloroform, bromoform and chlorbenzene mixed with CO_2 are at the same time characterized with the additional high-frequency asymmetry caused by increasing absorption. This asymmetry is also typical of the absorption bandshapes of diluted solutions of these compounds.

(4) No shift of the band maxima is observed through the entire pressure range of He, Ar and N_2. Only the maximum of the chloroform absorption band (ν_{max}=3034.5 cm^{-1}) is shifted to the high-frequency side when CO_2 is added. For a non-dipole naphthalene molecule, the frequencies of maxima of the absorption bands of vapours, their mixtures with foreign gases and solutions in neutral solvents practically coincide. Some of the studied absorption bands of vapours and their mixtures are shifted relative to the solution absorption bands to the high-frequency side. Thus, for the absorption band of chlorbenzene with ν_{max} = 1025.5 cm^{-1} this shift, as compared to the solution in CCl_4, is 1.5 cm^{-1}; for the chloroform absorption band with ν_{max}= 3034.5, it is 14.5 cm^{-1} and for the bromoform absorption band with ν_{max} = 3048 cm^{-1}, it is 18 cm^{-1}.

(5) Structureless, continuous contours of lighter molecules (C_2HCl_3, $CHCl_3$, $CHBr_3$) that appear in high pressure gas mixtures approach the solution contours in their half-widths. Continuous absorption bands of naphthalene mixed with foreign gases are still much wider (by a factor of 4-5) than those of the solution. But in all cases the shapes of the structureless vapour contours differ from the appropriate solution absorption bands.

(6) No change in the integrated intensity of the absorption bands of mixtures are observed throughout the test pressure range of foreign gases.

RESULTS AND DISCUSSION

The theoretical methods to calculate the dipole correlation functions (DCF) or directly the contours of vibrational-rotational absorption bands are proposed in [1,2]. The latter approach is more obvious although it is used more rarely than the former to compare theoretical and experimental data. Both approaches are employed in the present work.

The mathematical representation of the J-diffusion model for a symmetric-top molecule was made in [14,15]. The J-diffusion model calculation of the dipole correlation function $C_J(t)$ was performed by the following formula involving numerical evaluation of the multiple integrals as:

$$C_J(t) = \exp(- \frac{t}{\tau_J}) \sum_{n=0}^{\infty} \tau_J^{-n} \Big[\int_0^t C_0(t-t_n)dt_n \times \int_0^{t_n} C_0(t_n-t_{n-1})dt_{n-1} \cdots \int_0^{t_3} C_0(t_3-t_2)dt_2 \times \int_0^{t_2} C_0(t_2-t_1)C_0(t_1)dt_1\Big] \qquad (1)$$

where τ_J is the angular momentum correlation time, i.e. the time for which the angular momentum preserves its direction and magnitude. In (1) and below, the reduced times obtained by multiplying by $(kT/I)^{1/2}$ are used. The dipole correlation function $C_0(t)$ for a freely rotating symmetric-top molecules is defined by the following expression[16] applicable for the parallel band case:

$$C_0(t) = \frac{1}{2}(b+1)^{1/2} \cos\theta(z_4+z_5) \qquad (2)$$

where

$$z_4 = \int_{-1}^{1} (1-x^2)u^{-5/2}(u-t^2)\exp(-\frac{t^2}{2u})dx \quad ,$$

$$z_5 = \frac{2}{a}(1-a)^{1/2} - (\frac{2}{a^{3/2}})\sin^{-1}a^{1/2};$$

$$a = |b| \quad \text{at } b<0 \; ; \qquad u = 1 + \frac{1}{2}bx^2;$$

$$b = \frac{I}{I_z} - 1.$$

In [9,10], account is not taken of the possible relationship between the vibrational and rotational angular momenta. Therefore, the proposed model for rotational motion can be applied only to analyze parallel band contours. The dipole correlation function for perpendicular bands of freely rotating symmetric-top molecules is calculated by the formula allowing for the first-order Coriolis coupling constant, ζ,[17] in the expression for $C_0(t)$.

Figure 2 shows predicted $C_1(t)$ and experimental $C(t)$ obtained by the Fourier transformation of the appropriate absorption bandshapes of mixtures

$$C(t) = \int \hat{I}(\nu)\cos 2\pi(\nu-\nu_0)t d\nu$$

where ν are the vibrational-rotational frequencies of a given band, ν_0 is the vibrational transition frequency and $\hat{I}(\nu) = \frac{I(\nu)}{\int I(\nu)d\nu}$.

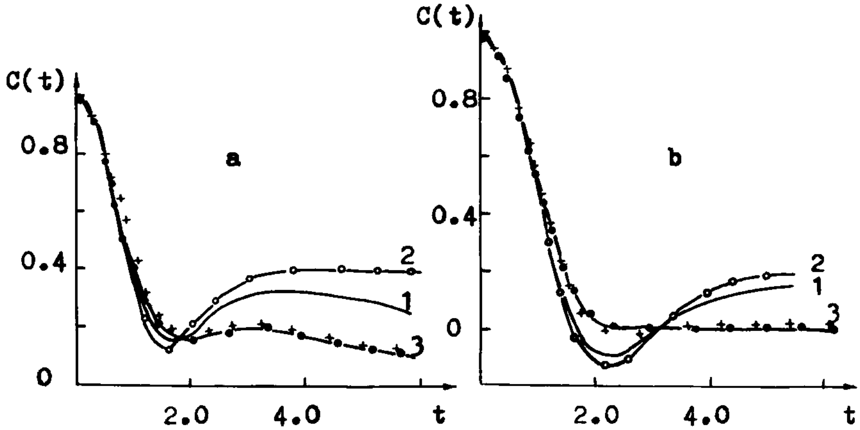

Fig. 2. Experimental and predicted correlation functions: a, experimental function for the absorption band of pure bromoform vapours (ν_{max}=3048.5 cm^{-1})(1); predicted function for free rotation (2); for vapours mixed with N_2 of 75 atm (3); function predicted by the J-diffusion model (x); b, experimental function for the absorption band (ν_{max}=1011.5 cm^{-1}) of pure naphthalene vapours (1); theoretical function for free rotation (2); for vapours mixed with CO_2 of 95 atm (3); function predicted by the J-diffusion model (x).

Figure 2a demonstrates a change in the rotational motion of bromoform about two equivalent axes perpendicular to the third-order symmetry axis when N_2 of 75 atm is added. Curve 1 shows the dipole correlation function of the absorption band of pure bromoform vapours, curve 2 gives the theoretical dipole correlation function for free rotation calculated by formula (2) and curve 3 is a plot of the experimental dipole correlation function of a mixture. Crosses at this curve indicate the values predicted by the J-diffusion model. When a foreign gas is absent, the dipole correlation function is similar to the one for free rotation and slowly damps at long times. In low-pressure vapours, unlike the solutions, the rotation slightly disturbed as compared to the free one is predominant in the absorption band contour formation. It has appeared that the theoretical dipole correlation functions predicted by the J-diffusion model well coincide with the experimental ones for high-pressure mixtures and somewhat worse for low-pressure ones when the Q-branch contributes much to the absorption band contour.

Figure 2b illustrates a change in the rotational motion of naphthalene about the perpendicular axes B and C of the molecule when CO_2 at 95 atm is added. The A-type absorption band is considered as a quasi-parallel one for a symmetric-top molecule since the naphthalene molecule is a heavy top with a small asymmetry parameter $\kappa = (2B-A-C)/(A-C) = -0.69$. In these cases, the asymmetry slightly distorts only the central part of the absorption band contour [18]. Theoretical and experimental dipole correlation functions are in good agreement over the entire pressure range of a mixture with CO_2 (0-95 atm).

The Fourier transformation of the theoretical correlation functions relates the intensity distribution, $I(\nu)$, in the vibrational-rotational absorption band contour both to the molecule parameters and to the time between molecule collisions as:

$$I_{J.M}(\nu) = \int_0^\infty C_{J.M}(t)\cos 2\pi\nu t\, dt \, . \tag{4}$$

However, calculations of the absorption bandshapes with the J-diffusion model were more conveniently carried out using the expressions[19] which require small computer time:

$$I_J(\nu) = \frac{A(\nu)[1-\beta A(\nu)]-\beta B^2(\nu)}{[1-\beta A(\nu)]^2 + \beta B^2(\nu)} \tag{5}$$

where

$$A(\nu) = \int_0^\infty \exp(-\beta t)C_0(t)\cos 2\pi\nu t \, dt,$$

$$B(\nu) = \int_0^\infty \exp(-\beta t)C_0(t)\sin 2\pi\nu t \, dt, \quad \beta = \frac{1}{\tau_J} .$$

The theoretical contours predicted by formulas (4) and (5) practically coincide.

In Fig. 3, the values of $I_J(\nu)$ obtained by the J-diffusion model with due regard for the 0-1 transition band contour of the considered vibration are plotted on the observed spectra of the absorption band (ν_{max}=1025.5 cm^{-1}) of chlorbenzene mixed with argon. At low pressures of Ar, the bandshapes predicted by the J-diffusion model satisfactorily display the variations of the contour but do not point to strong changes in the Q-branch region. In the case of 140 atm, the agreement with the observed contours is improved in the vicinity of the band maximum as well as on the low-frequency wing since with increasing foreign gas pressure the absorption band becomes more symmetric. The absorption band contours of chlorbenzene in argon at 140 atm are compared with those predicted by the J- and M-diffusion models. The calculation results obtained in terms of these models must approach when free rotation times are long. However, the contours predicted by the J- and M-diffusion models diverge for the test mixture, for which τ_J ranges from 4.16 to 0.96. At τ_J=0.96, this figure displays better representation of the absorption band

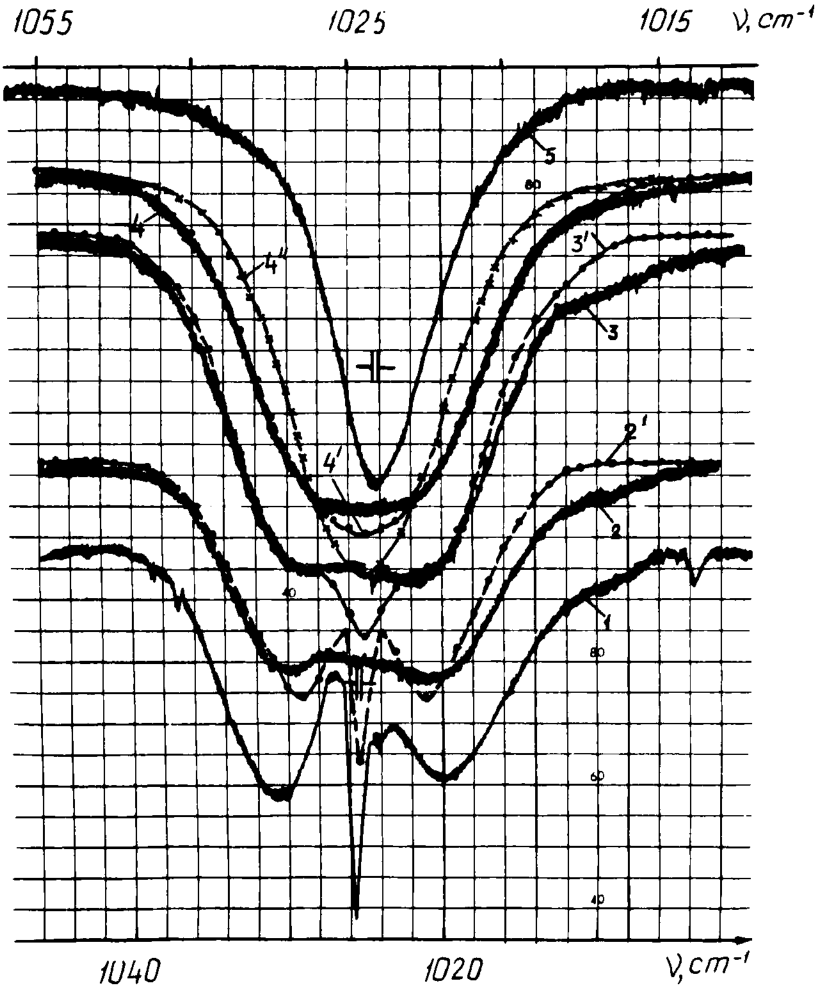

Fig. 3. Spectroscopic records of the absorption band of chlorbenzene vapours (1) and of vapours mixed with Ar of 40 atm (2), 80 atm (3) and 140 atm (4); 2', 3', 4', mixture absorption band contours predicted by the J-diffusion model; 4", by the M-diffusion model.

contour by the J-diffusion model than by the M-diffusion one.

The calculated values of $I_J(\nu)$ for the perpendicular absorption band of a symmetric-top molecule, including the Coriolis coupling constant, ζ,[17] are plotted on the observed absorption bands (ν_{max}=1220 cm^{-1}) of chloroform mixed with N_2 (Fig. 4). In the whole pressure range, the absorption band contours predicted by the J-diffusion model at ζ=0.96 satisfactorily display small changes of the band. The region of the band maximum changes with increasing pressure more slowly than it is predicted by theory. Under the same pressures, the perpendicular bands of chloroform and bromoform, as compared to the parallel ones, are much less affected by foreign gases.

The results obtained show that in the test pressure range the hindered rotation in dense gases is satisfactorily specified by the J-diffusion model. However, the calculation of the whole contour using τ_J alone is often difficult. The high- and low-frequency band wings are known to result from the "hot" molecule absorption, i.e. the band wings are formed due to radiation absorption by the molecules at high-lying rotational levels. The central part of the band develops due to absorption by "cooler" molecules[20]. Therefore, the central part of the band and its periphery, as is shown in[21], may broaden with increasing pressure in different ways because of different rotational relaxation rates of molecules participating in the band wings.

The calculations yield such an important parameter as the angular momentum correlation time, τ_J, that characterizes the changes in dynamics of the rotational motion at increasing pressure. The values of τ_J giving the best coincidence of the theoretical and experimental results obtained by formulas (1) and (5) may be interpreted as mean free rotation time at a given pressure. On the other hand, if the cross section of the collisions interrupting free rotation is close to the gas kinetic one, then the values of τ_J must correlate with

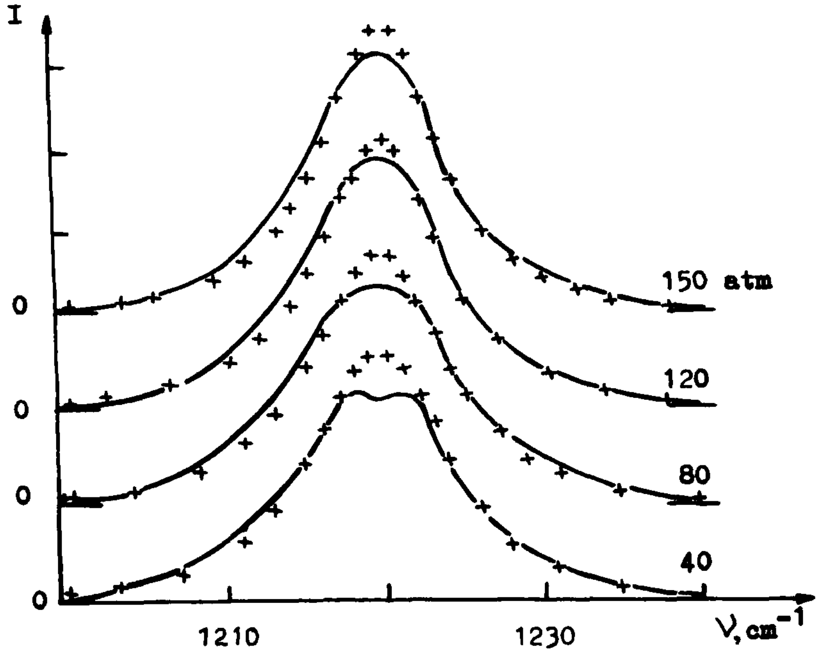

Fig. 4. Experimental and predicted absorption band contours of chloroform mixed with N_2.

mean times between the collisions in a gas mixture $\tau_{gas\ kin} = 1/z$ where z is the number of collisions per unit time. The values of τ_J and $\tau_{gas\ kin}$ (Table 1) are in good agreement, and the collision efficiency, ε, is close to 1, which is consistent with relatively strong collisions in a gas mixture.

The values of τ_J are a measure for diffusion steps. From the data presented it follows that already at short free rotation times corresponding to high pressure mixtures the molecules freely rotate through large angles between collisions. Thus, for bromoform mixed with N_2 of 175 atm, the time of free rotation about the axis perpendicular to the third-order symmetry axis is 0.8 of the mean rotation period, despite highly hindered

Table 1

Angular Momentum Correlation Times

Mixtures	P,atm	τ_J	$\tau_{gas\ kin}$	$\varepsilon = \frac{\tau_J}{\tau_{gas\ kin}}$
Bromoform + N_2	22	6	4.6	1.3
	50	3.57	2.68	1.3
	72	2.40	1.16	2.0
	175	0.99	0.68	1.45
Chlorbenzene + Ar	40	3.17	4.16	0.76
	80	1.58	2.56	0.62
	120	1.05	1.82	0.62
	140	0.90	0.96	0.93
Naphthalene+ CO_2	30	6.00	4.40	1.36
	63	1.60	1.39	1.15
	95	0.84	0.92	0.91

rotation displayed in a decrease of the angular momentum correlation time up to 1 picosecond.

For the contours of the perpendicular absorption bands of symmetric-top molecules, the intramolecular free rotation disturbances induced by the Coriolis forces prove to be predominant in the contour development and successfully compete with external disturbances due to collisions. Hence, the shapes of different perpendicular bands strongly depend on the Coriolis coupling constant, ζ, and slightly vary as τ_J decreases from 5 to 1 with increasing pressure of a foreign gas.

The results obtained show that the effect of increasing pressure of foreign gases on the band profiles is a result of transition from the free quantum rotation in vapours to the hindered one in compressed gas mixtures. The vibrational relaxation in the time range up to 5-6 picoseconds proves to be insignificant, i.e. it does not contribute much to the formation of the most part of the analyzed contours which extends from the wings up to $\nu_{max} \pm 2$ cm^{-1}. In the investigated pressure range, the contour transformation does not thus involve changes in the integrated intensity of absorption bands.

The analysis of some absorption bandshapes in solutions[22-24] shows that their differences from the structureless, continuous contours of gas mixtures are attributed to various relaxation processes which form the contours in two aggregate states. In a liquid phase, the molecules are characterized not only by another mode of molecular motion - reorientation, when the rotation angle at each single step is small and does not exceed several degrees, but also by more high vibrational relaxation rates than reorientational ones. As is shown in [22-24], for neutral solutions of bromoform and naphthalene, this is why in solutions the vibrational relaxation process is responsible for the most part of the width. Thus, for the absorption band (ν_{max} =1011.5 cm^{-1}) of naphthalene solutions the vibrational part of the width $\Delta\nu_{vib}$ is 2 cm^{-1}, for the band ν_{max} = 782 cm^{-1} it is 3 cm^{-1}, for the absorption band of bromoform solutions ν_{max}=3020 cm^{-1} it is 11 cm^{-1}, the complete band widths being 3.8, 5 and 16 cm^{-1}, respectively. Note that $\Delta\nu_{vib}$ obtained for solutions cannot be used to evaluate a vibrational broadening of the appropriate vapour bands. Large vibrational widths of liquid absorption bands are , to a considerable extent, attributed to additional channels for intermolecular relaxation processes, both phase and energy, observed in a liquid phase but absent in a vapour.

Thus, for the vapours and their mixtures with foreign gases at pressures no more than 200 atm the rotational relaxation is the dominating process that is responsible for the form of wide structureless absorption bands. The vibrational relaxation in these cases is a slower process and within a time range of several picoseconds is insignificant for the vibrational-rotational band.

REFERENCES

1. Gordon R.G. J. Chem. Phys., 1966, 44, 1830.
2. Pierre A.G., Steele W.A. Phys. Rev., 1969, 184, 172.
3. McClund P.E.D. Advances in Molec. Relax. and Interaction, 1977, 10, 83.
4. Herzberg G. "Vibrational and Rotational Spectra of Polyatomic Molecules", Izd. IL: Moscow, 1949, p. 648.
5. Allen H.C., Cross P.C. Molecular Vibrotor, 1963, No. 4, 200.
6. Gordon R.G. Adv. Magn. Resonance, 1968, 3, 1.
7. a) Bray R.C., Berry M.Z. J. Chem. Phys., 1979, 71, 4909;

   b) Berry R., Mohammadi Ali. Chem. Phys. Lett., 1980, 75, 99;

   c) West G.A., Mariella R.P., Pete J.A., Hammond W.B., Heller D.F. J. Chem. Phys., 1981, 75, 2006.
8. Sage M.L., Jortner J. Chem. Phys. Lett., 1979, 62, 451.

9. Borisevich N.A., Zalesskaya G.A., Shukurov T. DAN BSSR, 1978, 22, 600.

10. Borisevich N.A., Zalesskaya G.A., Shukurov. Zh. Prikl. Spektr., 1981, 34, 137.

11. Zalesskaya G.A., Shukurov T. DAN BSSR, 1982, 26, 288.

12. Borisevich N.A., Zalesskaya G.A., Shukurov T. Opt. i Spektr., 1982.

13. Shukurov T. Izv. AN BSSR, Ser. Fiz.-Mat. Nauk, 1981, No.3, 84.

14. McClung R.E.D. J. Chem. Phys., 1972, 57, 5478.

15. Pierre A.G., Steele W.A. J. Chem. Phys., 1972, 57, 4638.

16. Pierre A.G., Steele W.A., Phys. Rev., 1969, 184, 172.

17. Müller K., Kneubühl F. Chem. Phys., 1975, 8 468.

18. Hollas J.M. Spectrochim. Acta, 1966, 22, 81.

19. Bansal M.L., Rou A.P. Molec. Physics, 1979, 38, 1419.

20. Tolkachev V.A. Izv. AN SSSR, Ser. Fiz., 1968, 32, 1492.

Borisevich N.A., Zalesskaya G.A. Opt. i Spektr., 1974, 37, 72.

21. Burshtein A.I., Temkin S.I. Zh. Eksp. i Teor. Fiz., 1976, 71, 938.

22. Soussen-Jacob J., Dervil E., Vincent-Geisse J. Mol. Phys., 1974, 28, 935.

23. Zalesskaya G.A., Lastochkina V.A. Opt. i Spektr., 1978, 44, 504.

24. Zalesskaya G.A., Lastochkina V.A. Opt. i Spektr., 1979, 47, 306.

Received: October 6, 1982
Accepted: November 1, 1982