ROTATIONAL DIFFUSION OF GASEOUS CARBON DISULFIDE PERTURBED BY He, Ar AND N₂

By T. W. Żerda, A. Hacura, J. Żerda and E. Kluk

Institute of Physics, Silesian University, Katowice*

The angular position correlation functions, shortened to APCF, calculated from the $\nu_3(A_1)$ IR absorption band of CS_2 compressed with various gases were compared with those computed by the J-diffusion model. Not fully satisfactory fittings at low density and very accurate ones at high density were obtained. Also the values τ_J, which according to the J-diffusion model represent the average time between consecutive collisions, were compared with the time between collision — τ_{BC} for the hard sphere model.

1. Introduction

It is convenient to describe molecular motion in the Heisenberg picture. Gordon [1] has pointed out that a Fourier transform of absorption band shape $\varepsilon(\nu)$, in the infrared region, leads to the correlation function of the transition dipole moment $\vec{\mu}$

$$\phi(t) = \int_{-\infty}^{\infty} \varepsilon(\nu)e^{i2\pi c(\nu - \nu_0)t}d\nu = \langle \vec{\mu}(t)\vec{\mu}(0) \rangle. \qquad (1)$$

Since the change in the dipole moment $\vec{\mu}$ results from a variation in its direction $\hat{\mu}$ and in its length m, Eq. (1) can be written [2, 3] as follows:

$$\phi(t) = \langle \vec{\mu}(t)\vec{\mu}(0) \rangle = \langle \hat{\mu}(t)\hat{\mu}(0) \rangle \langle m(t)m(0) \rangle = G_{rot}(t)G_{vib}(t),$$

where $G_{rot}(t)$ and $G_{vib}(t)$ denote the rotational correlation function and the vibrational correlation function, respectively. In many recent papers [4–6], both phenomena were attracting a good deal of attention and a conclusion that for dilute gases in the picosecond time region $G_{vib}(t) = 1$ is drawn. Thus correlation function (1) describes rotational relaxation process only and consequently $\phi(t) = G_{rot}(t)$. In the gaseous phase linear molecules (like CS_2) give vibrational spectra which show significant rotational structure. With growing pressure of the perturbing gas the rotational line-widths appear to be con-

* Address: Instytut Fizyki, Uniwersytet Śląski, Uniwersytecka 4, 40-007 Katowice, Poland.

siderably larger than the distance between lines, so we observe a single broad band without any resolved fine structure. The purpose of the present article is to obtain a satisfactory interpretation of pressure effects on rotational motion of CS_2 with foreign gas mixtures.

2. Experimental

Infrared spectra of the ν_3 vibration-rotation band of CS_2 at a partial pressure of 120 mbar and compressed up to 300 bars by He, Ar, N_2 were recorded on a UR-20 spectrometer with a NaCl prism. The cylindrical high pressure cell (Fig. 1) constructed for this purpose of bronze berilium with CaF_2 windows 10 mm thick was used. The total pressure could be controlled to within a 0.5 bar accuracy. Gases were commercial products without further purification. The spectral resolution in our measurements was 5 cm⁻¹. For each
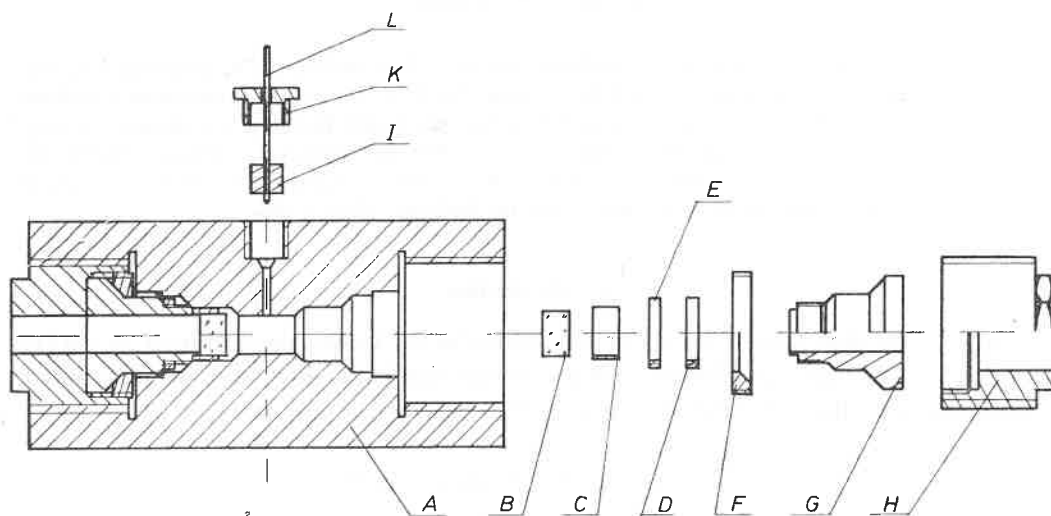

Fig. 1. Absorption cell for gases at high pressures. A — berylium bronze cell body, B — CaF_2 windows, C — adjusting ring, D — back nut, E — soft copper gasket, F — union nut, G — pressure seal position, H — screw plug, I — tapered inlet, K — union nut, L — capillary

set of physical conditions 15 runs were numerically averaged. In the investigated frequency region water has a strong absorption band. To prevent obscuration of the investigated band of CS_2 by atmospheric water vapour the spectrometer was dried by gaseous nitrogen. The molecule CS_2 has only three fundamentals, including one doubly degenerate. In nature sulfide appears mainly in the form of two isotopes ^{32}S and ^{34}S and that is why carbon disulfide has three isotopic species $^{12}C^{32}S_2$, $^{12}C^{32}S^{34}S$, $^{12}C^{34}S_2$, if the natural abundance of carbon isotope ^{13}C is neglected. Their relative intensities are estimated to be 450 : 40 : 1, respectively. The isotope shifts were estimated in the harmonic oscillator approximation [10]. For $^{12}C^{32}S^{34}S$ the band center is shifted about 7 cm⁻¹ whereas for $^{12}C^{34}S_2$ it is shifted 3 cm⁻¹ towards the low frequency end from the $^{12}C^{32}S_2$ band center.

At a temperature of 300°K about 15% of the CS_2 molecules are in the first excited vibration level ν_2. That is why near the main band of $^{12}C^{32}S_2$ at 1535.35 cm^{-1} the hot band at 1528.89 cm^{-1} is seen [7–9]. The method of calculating the correlation function from the CS_2 ν_3 band has been shown by Żerda [11].

3. The recalling on the extended diffusion model

In this paragraph the fundamental theoretical facts on molecular reorientation in gases, needed for interpretation of our experimental results, are recalled. The extended diffusion model of molecular reorientation in gases proposed by Gordon [12] and developed by others [13, 15] is based on the following assumptions:

1. The molecules undergo binary collisions only, with a negligible time of collision and between collisions they rotate freely.

2. After each collision the molecular angular momentum direction is randomized, whereas the angular momentum magnitude: a) remains constant (M-diffusion), b) changes (J-diffusion). In both cases the Maxwell-Boltzmann distribution of angular momentum is valid.

3. The time distribution of collisions for each molecule is given by a Poisson distribution.

It is worth noticing that the M-diffusion model exhibits some unphysical properties [14, 15], in spite of being successfully used to interprete experimental data for gaseous CO [12] and OCS [16]. For CS_2 experimental APCF courses are quite different from those predicted by the M-diffusion model. So we leave the M-diffusion model and concentrate on the J-model only.

The J-diffusion model, in the case of the dipole rotational correlation function, gives the following result [12]:

$$G_{\text{rot}}(t) = e^{-t/\tau_J} \sum_{n=0}^{\infty} \tau_J^{-n} \int_0^t \int_0^{t_n} \ldots \int_0^{t_2} F_0(t-t_n)F_0(t_n-t_{n-1}) \ldots F_0(t_2-t_1)F_0(t_1)dt_1 \ldots dt_n, \quad (2)$$

where $F_0(t)$ is the dipole rotational correlation function for a free rotating molecule and τ_J denotes angular momentum correlation time. In terms of the discussed model τ_J represents the average time between two consecutive collisions. If time t is given in so-called reduced units of $(kT/I)^{1/2}$, where I stands for the molecular moment of inertia, then $F_0(t)$ for a linear molecule has the form [12]

$$F_0(t) = \int_0^{\infty} \omega e^{-\omega^2/2} \cos (\omega t)d\omega. \quad (3)$$

In order to compute the correlation function (2) the traperoidal approximation by numerical integration is applied [12, 21].

If low density gas is taken into consideration, the quantum effects are important and the purely classical Gordon's model cannot be used. Moreover, the perspectives for the construction of the purely quantum model of molecular reorientation are rather faint. The only exception is the perfect gas of rigid rotors. Bliot [17], Eagles and McClung

[18] basing on this fact proposed a sort of semiquantum expression for APCF. They simply accepted formula (2) replacing the classical expression for $F_0(t)$ by its quantum counterpart.

4. Results

At low density the gaseous mixtures CS_2–He, CS_2–Ar and CS_2–N_2 present an absorption band with P and R branches separated by a gap. When the pressure of Ar or N_2 increases, the induced Q branch can be observed instead of the gap. In mixtures of CS_2–He the P and R branches remain even at 300 bars.

No frequency shift of the band's center is observed in the examined pressure region. The band intensity is given by the formula

$$A = \int_{band} \varepsilon(v)dv = \frac{1}{pl} \int_{band} \ln \frac{I_0(v)}{I(v)} \, dv,$$

where $I_0(v)$ and $I(v)$ are the transmittances at the frequency v of the base line and of the band, p is the density of the absorbing molecules and l is the absorption length. The band intensity does not change with the density of the perturber. The number of absorbing
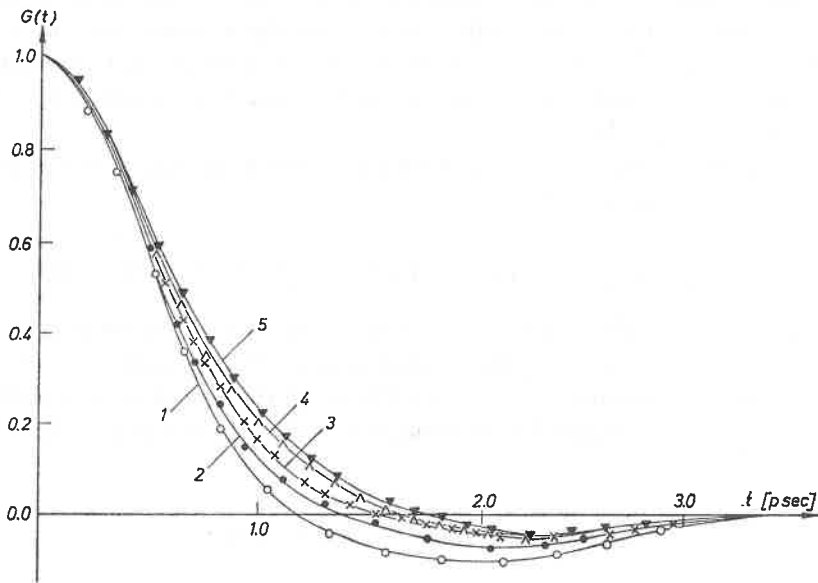

Fig. 2. Correlation functions for v_3 band CS_2 mixed with nitrogen at various pressures: *1* — pure, gaseous CS_2, *2* — 100 bars, *3* — 200 bars, *4* — 250 bars, *5* — 300 bars

molecules in the cell during measurements was, of course, in every case the same. It means that only the band shape is sensitive to the changes of foreign gas pressure. The best way of describing these changes seems to be the APCF method.

Figure 2 presents the correlation functions obtained for CS_2–N_2 mixtures with various nitrogen pressures. At low density correlation functions display a negative part with a significant minimum. This minimum decreases with increasing pressure. It may be expected that APCF would be all positive for nitrogen pressures greater than 300 bars. The measurements at pressures above 300 bars were not performed because of the compression strength of the CaF_2 windows.

A comparison between APCF's obtained at a total pressure 250 bars with various broadeners is presented in Fig. 3. The course of the APCF of gaseous CS_2 without any other gas at pressure 120 mbar is also marked.
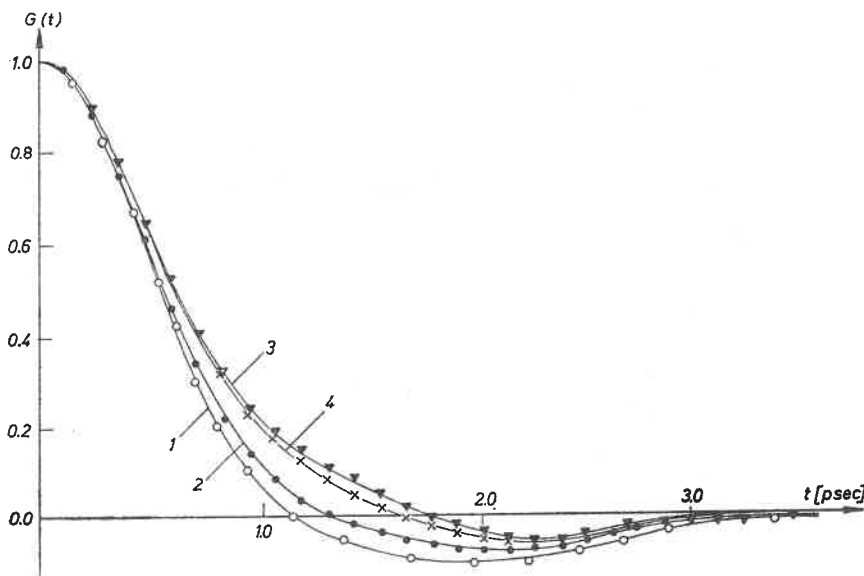

Fig. 3. Correlation functions for ν_3 band of CS_2. Total pressure 250 bars. *1* — pure CS_2, *2* — CS_2 + He, *3* — CS_2 + Ar, *4* — CS_2 + N_2

The analyses of Fig. 3 and of the modifications of the band shape indicate that helium is the weakest perturber and argon is stronger than nitrogen. The same result was confirmed for OCS by Clermontel et al. [4] and for CH_3D by Levi and Chalaye [6].

Even a simple comparison of the APCF plots for M-diffusion given by Gordon [12] with those plotted in Fig. 2 gave a very poor result.

Slightly better is the case of J-diffusion. It is possible to find the APCF, computed according to J-diffusion model, which gives a good fit to the experimental APCF. The examples with the best τ_J are shown in Fig. 4. In the low pressure region (up to 100 bars) it was impossible to find any compatibility between the model and the experimental APCF. In the case of CS_2 compressed by N_2 the fitting parameters τ_J giving the best results are assembled in Table I. The values of angular momentum correlation time τ_J for CS_2 perturbed by foreign gases at total pressure 250 bars are compared in Table II.

An attempt to calculate APCF using Eq. (2) with the quantum mechanical correlation function of a freely rotating molecule [11] was also made. In the high pressure region ($p \geqslant 200$ bars) the results are nearly the same as those obtained using the classical function
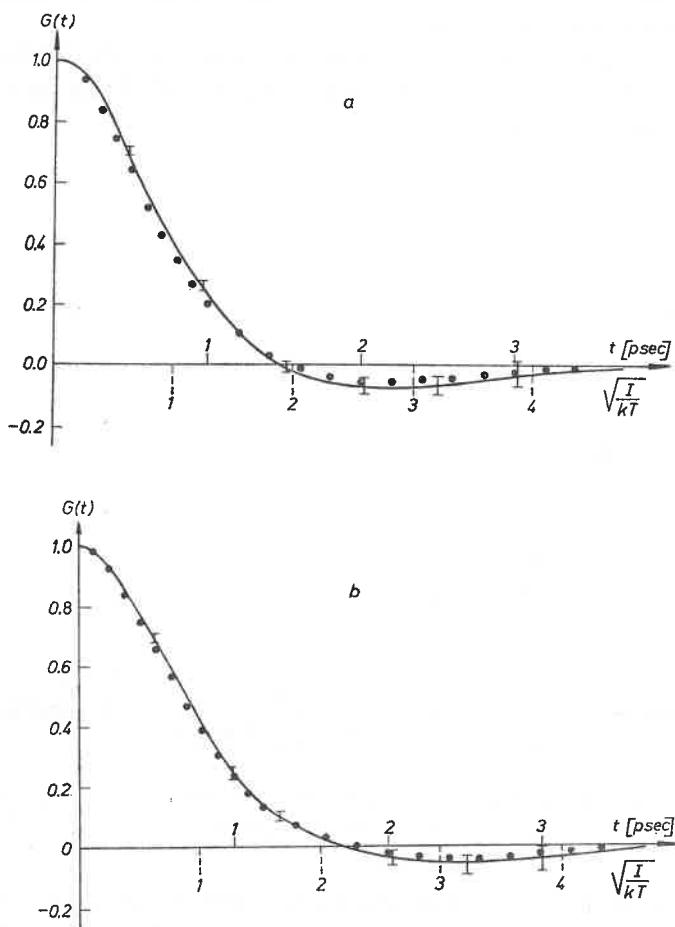

Fig. 4. Correlation functions of the CS_2–N_2 mixture. Full lines denote experimental APCF and crosses denote theoretical values of APCF. Note error bars. a) 250 bars, $\tau_J = 1.2$; b) 300 bars, $\tau_J = 0.95$

$F_0(t)$ (Eq. (3)). At lower pressures the curves of both theoretical APCF (classical and semiquantum) follow different courses and the difference increases with decreasing pressure. In the low pressure region the semiquantum APCF's are more similar to the experimental than the classical ones, but the fitting procedure cannot be applied — the differences are still too great.

In the J-diffusion model time τ_J has the meaning of the average time between collisions. These values are much shorter than may be expected. It is useful to compare them

TABLE I

Values of correlation times τ_J and time between collisions for gaseous CS_2 broadened by N_2 at various pressures

p(bar)	$\dfrac{\tau_J}{\left(\sqrt{\dfrac{I}{kT}}\right)}$	τ_J (psec)	τ_{BC} (psec)
0.120	*	*	2512
100	*	*	722
150	3.0 $\pm$ 0.5	2.346	535
200	2.0 $\pm$ 0.5	1.564	422
250	1.2 $\pm$ 0.1	0.938	346
300	0.95 $\pm$ 0.02	0.743	292

* unfitable.

TABLE II

Comparison of the values of the correlation times τ_J for CS_2 perturbed by foreign gases. Total pressure 250 bars

He	N_2	Ar
2.5	1.2	0.95

with the times between collisions τ_{BC} in the movable wall cell model [19]. According to this model for the mixture of two gases

$$\tau_{BC} = \frac{1}{\sqrt{\dfrac{8kT}{\pi m_1}} + \sqrt{\dfrac{8kT}{\pi m_2}}} \left[\left(\frac{1}{\varrho}\right)^{\frac{1}{3}} - \frac{1}{2}(\sigma_1 + \sigma_2) \right], \qquad (4)$$

where m_1, m_2 are molecular weights of both components; σ_1, σ_2 their diameters and T — temperature.

Density ϱ is calculated from Benedict's equation [20] but it also may be obtained directly from the pressure data given in the amagat units. The values $\sigma_{CS_2} = 4.4 \cdot 10^{-10}$ m [19] and $\sigma_{N_2} = 3.70 \cdot 10^{-10}$ m [20] are used in computing τ_{BC} for CS_2–N_2 mixtures (Eq. (4)); results are given in Table I.

5. Conclusions

At moderately high gas pressures ($p \leqslant 100$ bars) fitting procedure does not give satisfactory results. Neither classical nor semiquantum APCF's lead to a fairly good interpretation of molecular motion of gaseous CS_2. At higher pressures, when rotation is more frequently interrupted, rotational relaxation process becomes more classical than quantum mechanical and fits are better.

The fact that the times τ_J are about 200 times shorter than the times between hard collisions indicates that rotational motion is interrupted rather by long range intermolecular interaction than by mechanical hard collisions. It seems that the molecules are interacting for the longer spell of time, and the time interval, during which a molecule can be assumed to rotate freely, decreases to zero. Thus Eq. (2) cannot yield fully satisfactory results.

As far as we know, this paper is the first indicating that a linear molecule rotates approximately according to the *J*-diffusion model. Previous works [12, 16] pointed to the *M*-diffusion rather than to the *J*-diffusion process.

REFERENCES

[1] R. G. Gordon, *J. Chem. Phys.* **43**, 1307 (1965).
[2] S. Bratos, J. Rios, Y. Guissani, *J. Chem. Phys.* **52**, 439 (1970).
[3] L. A. Nafie, W. L. Peticolas, *J. Chem. Phys.* **57**, 3145 (1972).
[4] D. Clermontel, H. Vu, B. Vodar, *J. Quant. Spectrosc. Radiat. Transfer* **16**, 695 (1976).
[5] K. Muller, F. Kneubuhl, *Chem. Phys.* **8**, 486 (1975).
[6] G. Levi, M. Chalaye, *Chem. Phys. Lett.* **19**, 263 (1973).
[7] G. Blanquet, C. P. Courtoy, *Ann. Soc. Scient. Brux. I* **86**, 259 (1972).
[8] D. F. Smith, J. Overend, *Spectrochim. Acta* **26A**, 2269 (1970).
[9] D. Agar, E. K. Plyer, E. D. Tidwell, *J. Res. Natl. Bur. Stand.* **66A**, 259 (1962).
[10] G. Herzberg, *Molecular Spectra and Molecular Structure*, Van Nostrand, New York 1945.
[11] T. W. Żerda, *Acta Phys. Pol.* **A54**, 47 (1978).
[12] R. G. Gordon, *J. Chem. Phys.* **44**, 1830 (1966).
[13] A. G. St. Pierre, W. A. Steele, *J. Chem. Phys.* **57**, 4638 (1972).
[14] E. Kluk, *Mol. Phys.* **30**, 1723 (1975).
[15] R. E. D. McClung, *J. Chem. Phys.* **57**, 5478 (1972).
[16] C. Dreyfus, E. Dayan, J. Vincent-Geisse, *Mol. Phys.* **30**, 1453 (1975).
[17] F. Bliot, *Dissertation*, University of Lille, 1973.
[18] T. E. Eagles, R. E. D. McClung, *Chem. Phys. Lett.* **22**, 414 (1973).
[19] W. M. Madigorsky, T. A. Litovitz, *J. Chem. Phys.* **34**, 489 (1961).
[20] J. O. Hirschfelder, C. P. Curtiss, R.B. Bird, *Molecular Theory Gases and Liquids*, J. Wiley, New York 1954.
[21] R. E. D. McClung, *J. Chem. Phys.* **55**, 3459 (1971).