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DIPOLE MOMENT CORRELATION FUNCTION OF ν_3 BAND OF CS_2

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The correlation function for CS_2 is calculated taking into account the vibration-rotation interaction. Purely quantum mechanical formalism is applied. The Fourier transform of the infrared ν_3 band is corrected for shape changes due to isotope splitting and hot-bands. A method of calculating fractional intensity of hot bands is proposed. The experimentally obtained correlation function is compared to the theoretical one.

1. Introduction

The analysis of infrared contours can provide information about the rotational motions of the molecules in gases. The infrared band shape $I(\nu)$ is related to the time autocorrelation function [1]:

$$G(t) = \frac{\int\limits_{-\infty}^{\infty} I(\nu)\cos\left(2\pi c(\nu-\nu_0)t\right)d\nu}{\int\limits_{-\infty}^{\infty} I(\nu)d\nu}. \tag{1}$$

The extended diffusion models introduced by Gordon [2] were used to describe the reorientation of linear molecules. Compatibility between theory and experiment was observed. Cattani et al. [3, 4] showed that vibrational-rotational coupling cannot be neglected in the calculation of the theoretical correlation function. The aim of this paper is to state whether this interaction is important for the linear molecule, CS_2. The band at about 1535 cm^{-1} is studied in the gas-phase infrared spectrum.

2. Some data on molecular spectra of CS_2

The vibrational spectrum of carbon disulfide has been extensively studied [5–9]. The spectra of CS_2 are of interest since it is possible to observe the frequencies due to several isotopic species ($^{12}C^{32}S_2 \sim 90\%$; $^{12}C^{32}S^{34}S \sim 8\%$; $^{12}C^{34}S_2 \sim 1\%$; $^{13}C^{32}S_2 \sim 1\%$)

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and because with high resolution the l-type splitting in the bands can be obtained. Now we are in possession of accurate molecular constants of CS_2. They are assembled in Table I. It is known that CS_2, as any triatomic molecule, has only three fundamentals

$$\nu_1(00^00 \rightarrow 10^00) - 658.01\ \mathrm{cm}^{-1}$$

$$\nu_2(00^00 \rightarrow 01^10) - 395.98\ \mathrm{cm}^{-1}$$

$$\nu_3(00^00 \rightarrow 00^01) - 1535.35\ \mathrm{cm}^{-1}.$$

Numerical values are given for $^{12}C^{32}S_2$.

TABLE I

Molecular constants of $^{12}C^{32}S_2$ in cm^{-1} [6]

ν_3 band transition	ν_0	B'	B''	$D'_0 \times 10^8$
$(00^00 \rightarrow 00^01)$	1535.354	0.108399	0.109110	1.35
$(01^10 \rightarrow 01^11)_{\pi-}$	1528.896	0.108637	0.109349	1.0
$(01^10 \rightarrow 01^11)_{\pi+}$	1528.896	0.108564	0.109274	0.4

The main purpose of this work is to investigate the band centred at 1535.35 cm^{-1}. The band system at about 1535 cm^{-1} contains the ν_3 and $\nu_3+\nu_2-\nu_2$ bands of $^{12}C^{32}S_2$, $^{12}C^{32}S^{34}S$, $^{12}C^{34}S_2$, $^{13}C^{32}S_2$. The principal transition in this band system is $(00^00 \rightarrow 00^01)$ of $^{12}C^{32}S_2$. The influence of the $^{12}C^{34}S_2$ and $^{13}C^{32}S_2$ bands upon the total shape of the band system was neglected because they are very slight and shifted from the centre of $^{12}C^{32}S_2$ at the distance of about 7 cm^{-1} and 50 cm^{-1}, respectively. The isotope shift between $^{12}C^{32}S_2$ and $^{12}C^{32}S^{34}S$ is 3 cm^{-1}.

Each of $(00^00 \rightarrow 00^01)$ bands is accompanied by the so-called hot band $(01^10 \rightarrow 01^11)$. At the temperature of 300 K about 15% of CS_2 molecules have the upper state of ν_2 vibration excited. The interaction between vibrations ν_2 and ν_3 causes the shift equal to 6.45 cm^{-1} of the hot band in the direction of low frequency. The hot band spectrum is complicated by the l-type doubling and the resulting absorption corresponds to two sub-bands labelled π_+ and π_-.

3. *Calculation of the correlation function*

a. Transition $(00^00 \rightarrow 00^01)$

For nondegenerate parallel vibrations of linear molecules the positions of the lines in the P and R branches are represented by the equation

$$\nu = \nu_0+(B'+B'')m+(B'-B'')m^2-4D_0m^3, \tag{2}$$

where $m = -J$ for P branch $(\Delta J = -1)$, $m = J+1$ for R branch $(\Delta J = +1)$. An assumption that the centrifugal distortion constants D_0 are the same in the lower as in the upper states was made.

The theoretical correlation function of the dipole moment $\mu(t)$ relative to the transition $(v'' = 0 \rightarrow v' = 1)$ is given by the equation

$$G_{\text{quant}}(t) = \frac{1}{|\mu_{0\rightarrow 1}|^2} \sum_{J''J'} \varrho_{v''J''} |\langle J''v''|\vec{\mu}|J'v'\rangle|^2 \exp\left(2\pi c(\nu_{J''} - \nu_0)t\right), \tag{3}$$

$$\varrho_{v''J''} = \varrho_{v''}\varrho_{J''} = \frac{1}{Z_{\text{vib}}} \exp\left(-\frac{E_{\text{vib}}}{kT}\right) \frac{2J''+1}{Z_{\text{rot}}} \exp\left(-\frac{E_{J''}}{kT}\right).$$

Townes and Shawlow [11] gave the reduced expression for $\varrho_{v''}$ and $\varrho_{J''}$. The square elements can be separated into two independent parts, rotational and vibrational [10]

$$|\langle J''v''|\vec{\mu}|J'v'\rangle|^2 = |\langle J''|\hat{\mu}|J'\rangle|^2 |\mu_{0\rightarrow 1}|^2. \tag{4}$$

The matrix elements associated with the change in rotational quantum numbers from J'' to J' for linear rotators are given by

$$|\langle J''|\mu|J'\rangle|^2 = \begin{cases} \dfrac{J''+1}{2J''+1}; & J'' = J'+1 \\[2ex] \dfrac{J''}{2J''+1}; & J'' = J'-1. \end{cases} \tag{5}$$

Fig. 1 shows the theoretical $G_{\text{quant}}(t)$ calculated on the basis of Eq. (3), but the coupling between rotation and vibration was neglected — it means that in calculations of line positions (Eq. 2)) equality $B'' = B'$ was assumed. This result is compared with the classically obtained correlation function of a freely rotating molecule [2]

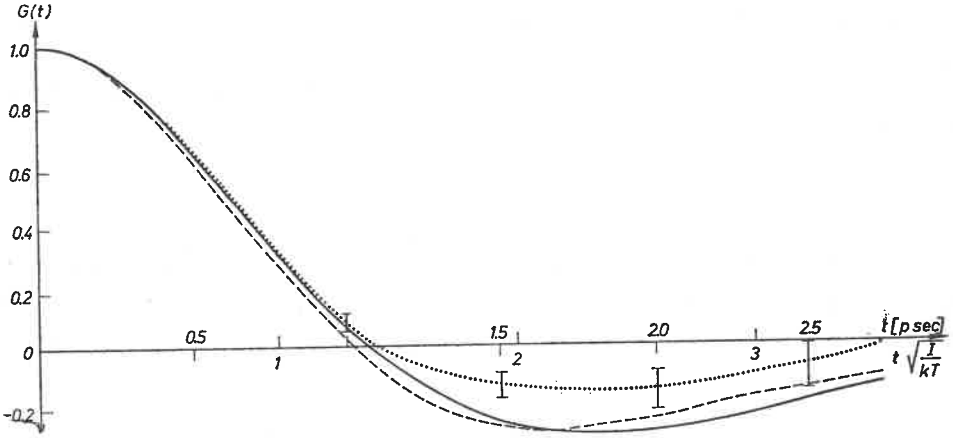

Fig. 1. Calculated and measured correlation functions od CS_2. The dotted curve gives the experimental function, the continuous curve shows the quantum correlation function with rotation-vibration coupling taken into account, the broken curve illustrates the curve of the classical correlation function as well as the quantum one without rotation-vibration coupling. Bars denote experimental errors

$$G_{\text{clas}}(t) = \int_0^\infty \cos(\omega t)\omega \exp\left(-\tfrac{1}{2}\omega^2\right) d\omega.$$

No difference in the shapes of the curves can be noted, and the dotted line denotes also a purely classical function.

b. Transition ($01^10 \rightarrow 01^11$)

For the hot band the quantum correlation function may be expressed as Eq. (3). But some modifications in Eqs (2) and (5) ought to be made. Assuming that the centrifugal distortion constants D_0 are the same in both vibrational states $v = 0$ and $v = 1$, the lines of each subband π_+ and π_- are given by the formula [8]

$$\nu = \nu_0-(B'-B'')+(B'+B''+4D_0)m+(B'-B'')m^2-4D_0m^3 \tag{6}$$

and

$$|\langle J''|\hat{\mu}|J'\rangle|^2 = \begin{cases} \dfrac{J''(J''+2)}{(J''+1)(2J''+1)}; & J'' = J'+1 \\ \dfrac{1}{J''(J''+1)}; & J'' = J' \\ \dfrac{J''^2-1}{J''(2J''+1)}; & J'' = J'-1. \end{cases} \tag{7}$$

The selection rules for this band allow for the transition $\Delta J = 0$. However, since this is a parallel band, the lines of the Q branch have an intensity that decreases very rapidly with increasing J [10]. The intensity of the Q branch was estimated — it is comparable to the individual line of the P or R branch.

The calculated correlation function of the hot band is identical with that of the main component (Fig. 1).

4. *Hot band and isotope shifts correction*

In order to obtain the experimental correlation function the Konynenburg and Steele method [12] can be applied. If the measured intensity at frequency ν is caused by different bands

$$I_{\exp}(\nu) = \sum_i x_i I(\nu-\nu_i), \tag{8}$$

where x_i is fractional intensity of the i-th component and ν_i — its center, then the Fourier transform of (8) leads to

$$G_{\exp}(t) = G(t)\,\{\sum_i x_i \cos(2\pi c(\nu_0-\nu_i)t)\}. \tag{9}$$

The basic assumption in this treatment is that all the components have the same line shape. Laulicht and Meirman [13] have extended relation (9) to the case of asymmetric bands.

Equation (8) is fulfilled by hot bands and isotope molecules of carbon disulfide. It was tested with the help of Eqs (2) and (5) for the main band and Eqs (6), (7) for the hot band.

The fractional intensities of the components were found by means of the Van Vleck and Weisskopf theory [11]. The band shape $I(\nu)$ is given by

$$I(\nu) = \sum_m k_m(\nu). \tag{10}$$

At the pressure of one atmosphere or less, the shape of an absorption rotation line, in the vinicity of ν_0, is described in good approximation by the Lorentz expression

$$k_m(\nu) = \frac{S_m}{\pi} \frac{\gamma_m}{(\nu_0^m - \nu)^2 + \gamma_m^2}, \tag{11}$$

where the line strength S depends on the quantum mechanical probabilities for radiative transitions and the population of the initial states (Eqs (5) and (7)), γ represents the half width of the line. From the examination of experimental results for the half width of [14], HCl [15], CO_2 [16], HCN [17] it may be concluded that with increasing m, γ increases to a maximum at m, which very often ranges from 3 to 10, and thereafter decreases nearly linearly. There is no literature data on half-widths in gaseous CS_2. Therefore we have assumed that γ in CS_2 (in the main band as well as in the hot band) are the same quantity as these in CO_2 and HCN, and that the variation with m is linear, changing from $\gamma = 0.1$ for $J = 2$ to 0.04 for $J = 100$. Such an estimation allows one to compute the band shape with Eqs (10) and (11).

Due to the l-type splitting the total shape of the hot band is twice as large as one might have concluded from (7) and from the fraction of the molecules in the first excited state of the ν_2 vibration. Transition ($01^10 \to 01^11$) has the same band shape as the ($00^00 \to 00^01$) one. These results do not depend on the way of choosing the γ values. When $\gamma = 0.1$ for all J, the calculated shape differs only in details from the one obtained with γ changing linearly from 0.1 to 0.04. Here we are not looking for the best fit of the calculated spectrum with the observed one, so such a comparative method is quite satisfactory when the ratio of the main band intensity to the hot band intensity is only needed. The assumption that lines numbered with the same J have the same half-widths (despite they belong to different transitions) seems to be correct. Thus the discussed ratio is not varying with frequency. $|\mu_{0\to1}|^2$ of the main band (4) was assumed to be the same as that of the hot band.

The addition of intensities of all components — main and hot bands of $^{12}C^{32}S_2$ as well as $^{12}C^{32}S^{34}S_2$ — falls short for comparing the calculated total intensity with the experimentally obtained band shape. The true band shape is modified by the instrument function. The instrument function includes some distorting factors, from which the optical distortion is often the greatest source of changes in the true band intensity. The influence of instrumental optics on the spectra is expressed in a succinct form [18]

$$I_m(\nu) = (I_t * S)(\nu), \tag{12}$$

where I_m is the distorted intensity, assumed to be identical with the measured one, I_t is the true intensity, S is so-called slit function, and the asterisk denotes convolution.

The spectrum of the ν_3 band of CS_2 was measured by the use of the UR-20 spectrophotometer with a slit of 5 cm^{-1}. In this case the slit function can be given in the form of a triangular function. True band intensity was assumed to be the sum of all compound and the convolution (12) was calculated numerically. On Fig. 2 we can see the result. The four components, each corrected by the slit function, are also shown. Now, the fractional intensities x_i, necessary for the calculation of the correlation function (9), may be obtained. Here they are:

$$^{12}C^{32}S_2\ (00^00 \rightarrow 00^01) \qquad x_1 = 0.7123 \qquad \Delta\nu_1 = 0$$

$$(01^10 \rightarrow 01^11) \qquad x_2 = 0.2137 \qquad \Delta\nu_2 = -6.45\ \mathrm{cm}^{-1}$$

$$^{12}C^{32}S^{34}S\ (00^00 \rightarrow 00^01) \qquad x_3 = 0.0570 \qquad \Delta\nu_3 = -3.0\ \mathrm{cm}^{-1}$$

$$(01^10 \rightarrow 01^11) \qquad x_4 = 0.0170 \qquad \Delta\nu_4 = -9.45\ \mathrm{cm}^{-1}.$$

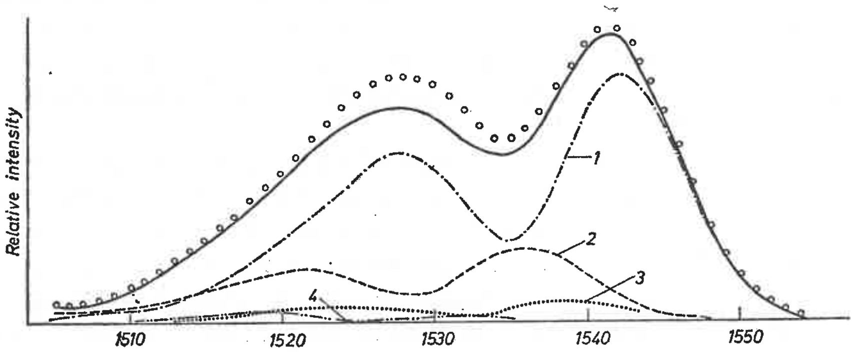

Fig. 2. This figure gives a comparison of the measured spectrum (crosses) with the calculated one (continuous curve) of CS_2 in gaseous phase. The four components are also shown, *1* — denotes the main band of $^{12}C^{32}S_2$;*2* — denotes the hot band of $^{12}C^{32}S_2$; *3* — denotes the main band of $^{12}C^{32}S^{34}S$; *4* — denotes the hot band of $^{12}C^{32}S^{34}S$

The differences between the observed and calculated intensities (Fig. 2) are not too pronounced, except for the frequency region, viz. from 1526 cm^{-1} to 1532 cm^{-1}. This may be due to the choice of γ values inadequate to reality. The result of the present procedure, which neglects all details of line broadening and concentrates on a very simple theory, is sufficient.

The correlation function obtained from the measurements according to (1) was corrected by taking into account the slit function (12), isotopic splittings and hot bands (9). The result is plotted in Fig. 1. There is compatibility between experiment and quantum theory, where rotation-vibration coupling was taken into consideration, for times up to 1 psec. For longer time periods the curves go various ways and differences are greater than experimental errors.

5. Summary

The correction for hot bands cannot be made taking into consideration the thermal excitation only. When the lower state of the hot band is the doubly degenerated state and if the lines are located close one to another, the hot band shape is twice as large as it results from the Boltzmann distribution (Eq. (3)).

It was shown (Fig. 1) that despite the character of the transition, whether it is the main band or the hot band, quantum correlation functions have the same shape.

Quantum correlation functions were calculated in two variants with and without rotation-vibration interaction. When the coupling was neglected an ideal compatibility with classical correlation function was obtained. The comparison with experimental result shows that this interaction is important and cannot be neglected.

In Gordon's model of the rotational diffusion process [2] the rotational motion was described by classical mechanics. The classical rotation model predicts symmetrical band contours. The assumption that there is no vibration-rotation interaction ($B' = B''$ in Eq. (2)) leads also to symmetrical band contours, so the asymmetry of the spectral band is quantum mechanical in origin. The application of Gordon's model is valid in the case of symmetrical band only. Spectra of molecules in the gaseous phase are always asymmetrical about the band center. This asymmetry disappears with increasing pressure, thus the classical model seems to be valid in the high pressure region.

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