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VIBRATIONAL ANHARMONICITY OF CARBON DUSILPHIDE
MOLECULES IN SOLUTION

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The infrared and Raman spectra of a one per cent solution of carbon disulphide in carbon tetrachloride were analysed. From ten chosen transitions, the three zero-order frequencies and seven anharmonicity constants were derived. Comparison with the corresponding values of CS_2 in vapour and liquid states shows that the solution data take an intermediate position in most cases, indicating a real change of these constants on dissolution and liquefaction. The Fermi resonance constant does not seem to be appreciably affected by the changes of state.

Parameters defining the anharmonicity of molecular vibrations are known for a relatively small number of simple molecules. These data are derived from vibrational frequencies of the substances in their gaseous states. The question of whether anharmonicity constants change on dissolution has been first considered by Burneau and Corset [1] and Choppin and Downie [2] in the case of dissolved water. Conclusions of both works were that anharmonicity constants derived from the vapour state can be applied to solution spectra. An independent investigation of Ribnikar and Pužić [3] on liquid carbon disulphide concluded that five of seven anharmonicity constants do not change on condensation within the limits of error of band frequency determinations. The practical identity of anharmonicity constants in gaseous and dissolved states was later found also by Ribnikar *et al.* [4] in two carbon dioxide solutions and by Downie and Choppin [5] in solutions of H_2O and D_2O .

Since infrared spectra of carbon disulphide dissolved in inert solvents were known to exhibit relatively sharp bands [3], enabling thus rather precise band frequency determinations, it seemed worth while to analyse this and the Raman spectrum in detail and to compare the resulting anharmonicity constants with the known data of the vapour and liquid states.

EXPERIMENTAL

Reagent grade carbon disulphide was dissolved in dried carbon tetrachloride. Infrared spectra of the solution were recorded in the range of 300 to 6000 cm^{-1} employing the grating spectrophotometers Perkin-Elmer 457 or 521 and the Beckman DK—1A, equipped with a quartz prism. The Raman spectra were excited with a Spectra Physics argon-ion laser, model 164—03, employing the 514.5 nm line. A Spex double monochromator 1401 with a thermoelectrically cooled photon counter was employed.

The concentration of CS_2 was one volume per cent except for the weakest bands where series of higher concentrations were recorded with subsequent extrapolation to one per cent.

For calibration of frequency scales in the infrared, atmospheric ammonia and polystyrene film absorption was employed, according to Downie *et al.*[6]. The Raman spectrum was calibrated by the simultaneously recorded solvent bands.

The measured frequencies of the main bands with their assignments are listed in Table I, referring to ambient temperatures of the instruments. The decimals of the wave numbers, when given, do not reflect the true accuracy of measurements. They were retained after averaging or extrapolation even though the estimated uncertainties in many cases exceeded one wave number. The cause of this, besides the great natural width of the bands, was a slight temperature dependence of band frequencies which was unfortunately neglected to be taken into account.

ANALYSIS OF THE SPECTRUM

Most of the bands in the spectrum of dissolved carbon disulphide show more or less resolved hot bands, mostly on their red sides. Three of such bands have been subjected to analysis in a previous work [3]. Their band maxima were remeasured with increased accuracy and an attempt was made to resolve the rest graphically. Calculated Lorentzian bands of appropriate band-widths, including the isotopic sub-bands, were subtracted from the measured band contours. In most cases the strongest hot bands, arising from the level 01^10 , could be separated clearly. To a smaller extent the transitions involving the level 10^00 could be distinguished by their smaller band-width. The remainder of hot bands was in most cases difficult to assign unambiguously. Besides the crowding of bands, the reason are quite anomalous intensities encountered, which in many cases do not follow the expected Boltzmann populations of their lower levels.

The band of ν_2 , as appearing in solution, is shown on Fig. 1a. Two side-bands are seen. The stronger one shows a positive displacement of 9.4 cm^{-1} . Its integrated intensity was found to be between 21 and 26% of the main band. We believe it to be the transition 02^00 — 01^10 despite the intensity which is somewhat lower than expected for such a transition (30%). The energy of the level 02^00 is found from this difference band. The other side-band on the low frequency side is very probably 11^10 — 10^00 .

TABLE I
Observed transitions of CS₂ in 1% solution in CCl₄

Frequency	Intensity ^a	Spectrum	Transition	Species
395.2	s.	IR	01 ¹ 0—00 ⁰ 0	Π _u ⁺ —Σ _g ⁺
655.6	s.	R	10 ⁰ 0—00 ⁰ 0	Σ _g ⁺ —Σ _g ⁺
799.8	s.	R	02 ⁰ 0—00 ⁰ 0	Σ _g ⁺ —Σ _g ⁺
1521.9	v.s.	IR	00 ⁰ 1—00 ⁰ 0	Σ _u ⁺ —Σ _g ⁺
2168.5	s.	IR	10 ⁰ 1—00 ⁰ 0	Σ _u ⁺ —Σ _g ⁺
2308.8	m.	IR	02 ⁰ 1—00 ⁰ 0	Σ _u ⁺ —Σ _g ⁺
2815.9	m./w.	IR	20 ⁰ 1—00 ⁰ 0	Σ _u ⁺ —Σ _g ⁺
2945.0	w.	IR	12 ⁰ 1—00 ⁰ 0	Σ _u ⁺ —Σ _g ⁺
3115.8	v.w.	IR	04 ⁰ 1—00 ⁰ 0	Σ _u ⁺ —Σ _g ⁺
3464.6	v.w.	IR	30 ⁰ 1—00 ⁰ 0	Σ _u ⁺ —Σ _g ⁺
4525	v.w.	IR	00 ⁰ 3—00 ⁰ 0	Σ _u ⁺ —Σ _g ⁺
387.8	w., sh.	IR	11 ¹ 0—10 ⁰ 0	Π _u ⁺ —Σ _g ⁺
404.6	w.	IR	02 ⁰ 0—01 ¹ 0	Σ _g ⁺ —Π _u ⁺
642.3	w.	R	12 ⁰ 0—02 ⁰ 0	Σ _g ⁺ —Σ _g ⁺
648.1	m.	R	11 ¹ 0—01 ¹ 0	Π _u ⁺ —Π _u ⁺
653.0	w.	R	20 ⁰ 0—10 ⁰ 0	Σ _g ⁺ —Σ _g ⁺
			12 ⁰ 0—02 ⁰ 0	Σ _g ⁺ —Δ _g
865.5	m.	IR	00 ⁰ 1—10 ⁰ 0	Σ _u ⁺ —Σ _g ⁺
1512.0	m., sh.	IR	10 ⁰ 1—10 ⁰ 0	Σ _u ⁺ —Σ _g ⁺
1515.4	m., sh.	IR	01 ¹ 1—01 ¹ 0	Π _g ⁺ —Π _u ⁺
2155.0	m., sh.	IR	11 ¹ 1—01 ¹ 0	Π _u ⁺ —Π _g ⁺
2289	w., sh.	IR	12 ⁰ 1—10 ⁰ 0	Σ _u ⁺ —Σ _g ⁺
2793.9	w.	IR	21 ¹ 1—01 ¹ 0	Π _u ⁺ —Π _g ⁺
2803.4	w., sh.	IR	30 ⁰ 1—10 ⁰ 0	Σ _u ⁺ —Σ _g ⁺
2926	v.w., sh.	IR	22 ⁰ 1—10 ⁰ 0	Σ _u ⁺ —Σ _g ⁺
4504	v.w., sh.	IR	01 ¹ 3—01 ¹ 0	Π _g ⁺ —Π _u ⁺
1472.3	m./w.	IR	¹³ C 00 ⁰ 1—00 ⁰ 0	Σ _u ⁺ —Σ _g ⁺
646.2	m.	R	³⁴ S 10 ⁰ 0—00 ⁰ 0	Σ _g ⁺ —Σ _g ⁺
2155	m.	IR	³⁴ S 10 ⁰ 1—00 ⁰ 0 ^b	Σ _u ⁺ —Σ _g ⁺
2793	w.	IR	³⁴ S 20 ⁰ 1—00 ⁰ 0 ^b	Σ _u ⁺ —Σ _g ⁺
3432	v.w.	IR	³⁴ S 30 ⁰ 1—00 ⁰ 0 ^b	Σ _u ⁺ —Σ _g ⁺

^a. s. — strong, m. — medium, w. — weak, v. — very, sh. — shoulder

^b. Overlapped with C³²S₂ ν₁ 0⁰1—01¹0.

The relative intensity of the band of ν₁, which is seen in the infrared spectrum of liquid CS₂, diminishes rapidly on dissolution. In addition, it appears in a region of strong solvent absorption, and it could not be detected in dilute solutions. It appears in the Raman spectrum clearly, as shown in Fig. 2. It is also accompanied with a multitude of hot bands, the strongest one originating from 01¹0 with a relative intensity of 0.24.

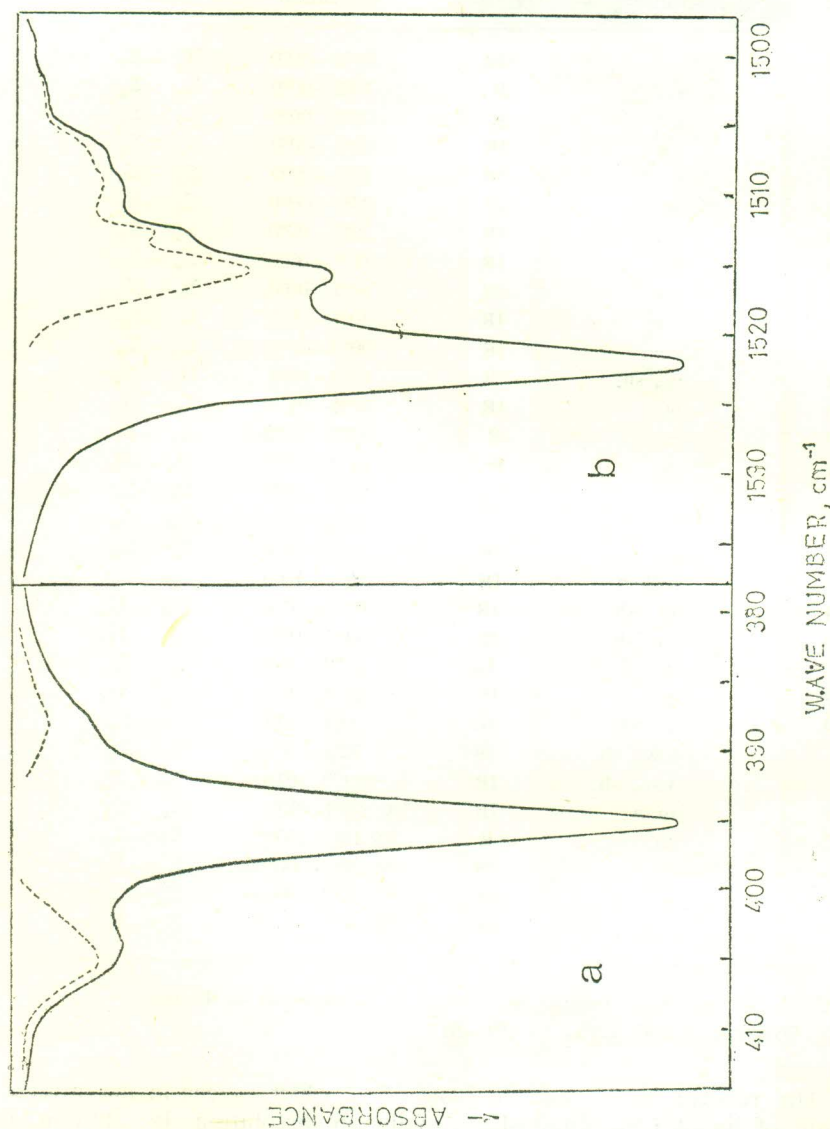


Fig. 1. The two infrared active fundamentals of CS_2 in 1% solution. a— ν_2 , b— ν_3 . Broken lines are residues after subtracting the contributions of the main bands including ^{33}S and ^{34}S sub-bands.

The band of ν_3 was remeasured, giving a frequency of 1521.9 cm⁻¹ for its absorption maximum. This band has a series of incompletely resolved hot bands on the low frequency side, as shown in Fig. 1b. The band which could be most reliably separated by graphical means shows a displacement of -6.5 cm⁻¹, representing the transition 01¹—01⁰.

The hot bands accompanying the transitions 10⁰1—00⁰0 and 20⁰1—00⁰0 have been analysed in Ref. 3. The intensities of their hot bands, including 00⁰1—00⁰0, were remeasured with results shown in Table II.

The hot bands associated with 02⁰1—00⁰0 and 04⁰1—00⁰0 are difficult to separate because of their closeness to the main bands. The same applies to 12⁰1—00⁰0, which is for example seen in Fig. 3 at 2945 cm⁻¹. The only definable feature on its red side arises very probably from 22⁰1—10⁰0.

The band found at 4525 cm⁻¹ is assigned as 3 ν_3 and its side-band, displaced for -21 cm⁻¹, as 01¹3—01¹0.

The infrared spectrum of *liquid* carbon disulphide has been thoroughly analysed in Ref. 3. The only change was made in the frequency of ν_3 . The frequency quoted, 1508 cm⁻¹, was obviously erroneously determined both because of strong atmospheric absorption in the region of its peak maximum and of its very high intensity. One previously unassigned band accompanying it was recognised as the ¹³C-band, which is presently measured as 1472.3 cm⁻¹. Adding to this frequency of the calculated isotopic shift of 49.7 cm⁻¹, a new value of 1512 cm⁻¹ is obtained for the main band.

TABLE II

Relative intensities of hot bands associated with transitions
00⁰1—00⁰0, 10⁰1—00⁰0 and 20⁰1—00⁰0

Transition	Intensity predicted	Intensity found		
		$\nu_1 = 0$	$\nu_1 = 1$	$\nu_1 = 2$
ν_1 0 ⁰ 1—00 ⁰ 0	1.000	1.00	1.00	1.00
ν_1 1 ¹ 1—01 ¹ 0	0.300	0.31	0.29*	0.30*
ν_1 2 ⁰ 1—02 ⁰ 0	0.065	0.10	0.108	0.11
ν_1 3 ¹ 1—03 ¹ 0	0.012	0.02	0.024	0.026
ν_1 4 ⁰ 1—04 ⁰ 0	0.002		0.0087	

* ¹²C³²S³⁴S bands subtracted

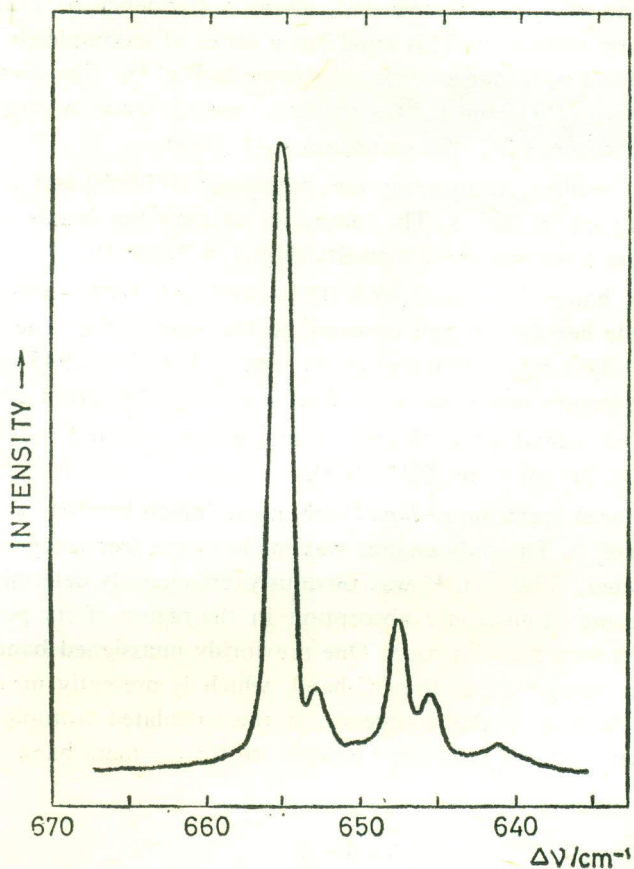


Fig. 2. The ν_1 band system in the Raman spectrum of CS_2 in 5% solution in CCl_4 . Effective slit width 1.0 cm^{-1} , laser power 0.8 W .

CALCULATION OF THE ANHARMONICITY CONSTANTS

In order to obtain the three zero-order (harmonic) frequencies and the seven anharmonicity constants, ten appropriately chosen term values are to be known. For the present purpose the system developed for CO_2 , described in Ref. 4, was applied to both dissolved and liquid CS_2 data. The ten frequencies chosen are marked with asterisks in Table III. The value of 36 cm^{-1} for the Fermi resonance interaction constant was applied in both cases. The relationship

$$W^2 = (36)^2 \frac{1}{4} [(v_2 + 2)^2 - I_2^2] v_1$$

was applied in the perturbation calculations. Unperturbed energies of the levels were then found and the anharmonicity parameters calculated. These results are shown in Table III, together with the most recent values [7] for gaseous CS_2 .

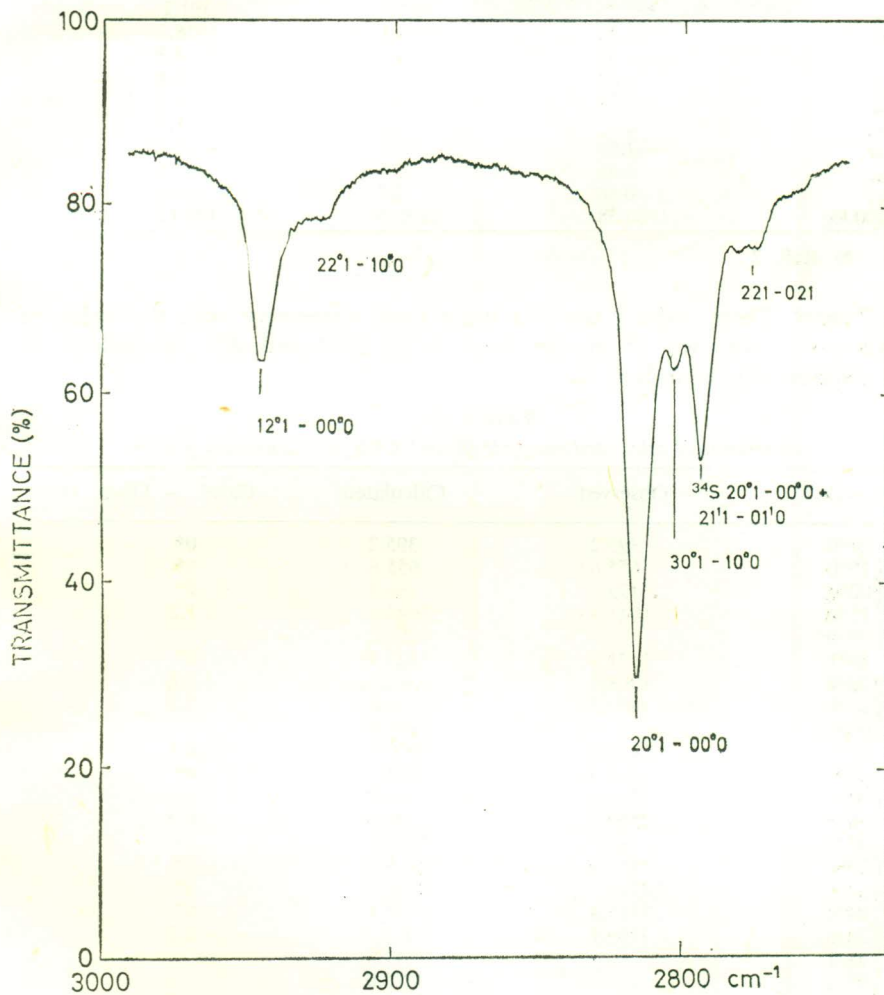


Fig. 3. The system of 20^1-00^0 and 12^1-00^0 in 5% solution. Cell thickness 10 mm.

In the case of solution data two additional checks were at hand for the value of the constant x_{23} . The difference between the peaks of 01^1-01^0 and ν_3 gives directly its value, which was found to be $-6.5\ \text{cm}^{-1}$. In a similar manner, the difference between 01^1-01^0 and $3\nu_3$ equals $3x_{23}$, yielding

TABLE III

Harmonic frequencies, anharmonicity constants and zero-point energies of vapour phase, dissolved and liquid carbon disulphide (units: cm^{-1})

Constant	Vapour*	Solution	Liquid
ω_1	672.71	665.6	658.7
ω_2	398.26	395.0	391.2
ω_3	1558.71	1546.4	1538.7
x_{11}	-1.02	0.9	4.3
x_{22}	1.09	0.6	1.4
x_{33}	-6.54	-6.8	-6.2
x_{12}	-2.9	2.2	1.1
x_{13}	-7.66	8.7	-11.7
x_{23}	-6.45	-6.6	-8.5
g_{22}	0.88	0.7	-1.1
$G(0000)$	1506.58	1495.7	1484.2

*) Ref. 7

-6.7 cm^{-1} . These values are in a quite good agreement with the value of -6.6 cm^{-1} obtained from the levels 02⁰1, 02⁰0 and 00⁰1, according to the relation (7) from Ref. 4.

TABLE IV

Observed and calculated energy levels of $^{12}\text{C}^{32}\text{S}_2$ in 1% solution (cm^{-1})

Level ^a	Observed	Calculated	Calcd. — Obsd.
01 ¹ 0	395.2	395.2	0*
[10 ⁰ 0	655.6 ^b	655.6	0*
[02 ⁰ 0	799.8	799.8	0*
[11 ¹ 0	1043.4 ^c	1044.6	+1.2
[03 ¹ 0		1206.2	
00 ⁰ 1	1521.9	1521.9	0*
[20 ⁰ 0	1308.6	1312.2	+3.6
[12 ⁰ 0	1442.1	1445.8	+3.7
[04 ⁰ 0		1620.0	
01 ¹ 1	1910.6	1910.5	-0.1
[10 ⁰ 1	2168.5	2168.5	0*
[02 ⁰ 1	2308.8	2308.8	0*
[11 ¹ 1	2550.2	2550.6	+0.5
[03 ¹ 1		2708.7	
[20 ⁰ 1	2815.9	2815.9	0*
[12 ⁰ 1	2945.3	2945.3	0*
[04 ⁰ 1	3115.8	3115.8	0*
[21 ¹ 1	3189.1	3191.3	+2.2
[13 ¹ 1		3341.4	
[05 ¹ 1		3525.0	
[30 ⁰ 1	3464.6	3463.4	-1.2
[22 ⁰ 1	3577	3582.6	+5.6
[14 ⁰ 1		3745.8	
[06 ⁰ 1		3939.0	
00 ⁰ 3	4525	4525.0	0*
01 ¹ 3	4899	4900.2	+1.2

^a. Levels connected with brackets are in Fermi resonance.

^b. Infrared value 656.4 from 00⁰1—10⁰0.

^c. Raman value 1043.3 from 11¹0—01¹0.

*) Frequencies taken to calculate anharmonicity constants,

By using the derived constants, unperturbed energies of other levels were calculated. After the perturbation calculation (when applicable) the results were compared with experimentally obtained levels not involved in the setting of the system. These results are given in Table IV.

DISCUSSION

When treating a solution spectrum having bands of half-widths of the order of 5 cm⁻¹ or more, determination of precise positions of their maxima is quite limited. Overlapping of closely laying hot bands with the main peak can also introduce displacements in the maxima. Solvent-solute interactions make sometimes the band frequencies temperature dependent. All these facts contribute to an uncertainty in the true band positions. Adding purely instrumental errors, it can amount to one wave number or more in the present case. In addition, there are no data on the influence of the change of state on the magnitude of Fermi resonance. The result is a quite large error associated with the derived anharmonicity constants. To our estimation it might range from ± 5 cm⁻¹ in the case of x_{12} to ± 0.2 for x_{33} .

Comparison of the data of the vapour phase, dissolved and liquid state of CS₂, listed in Table III, leads to a conclusion that, despite the large expected uncertainties, the constants of dissolved CS₂ take in most cases positions intermediate to the two extremes. The only clear exception are x_{12} and g_{22} , where the solution constants are quite above the average of the gaseous and liquid values. Although there might be some fundamental reason for it, we believe rather in the result of accumulated errors which make these two constants especially sensitive.

The question of constancy of the quantum mechanical resonance constant, W , is worth of consideration. From the frequencies available its value could not be directly determined.*

As mentioned above, both dissolved and liquid data were treated with the same value of $W = 36$ cm⁻¹. An attempt was made to change the constant by both increasing it in the sequence vapour — solution — liquid, keeping the vapour phase data constant and the solution data intermediate. The agreement between the calculated frequencies and the observed ones available for checking became in both cases worse, but not seriously so up to a change of ± 5 cm⁻¹. Larger changes lead to situations where e.g. harmonic frequencies become larger in the liquid than in the vapour or produced switches in the triad levels, both of which do not seem to be realistic. One may therefore conclude that dissolution and condensation have only a small effect on the resonance constant W .

The confusing situation of anomalous intensities of hot bands in the spectra has also been noticed by Giguere *et al.*[8] in the vapour phase spectrum of the CS₂ transition 04⁰1—00⁰0. These authors advanced an explana-

* It should be noted that the equation for explicit derivation of W in Ref. 3 contains a typographical error. In the third part of Eq. (3) instead of „ $p =$ “ it should read „ $p^2 =$ “. It was also omitted to mention that p^2 equals to $x_{12} - 2x_{23}$. In the present case this relation could not be applied due to the lack of suitable levels.

tion of this phenomenon as changed transition probabilities due to mixing by Fermi resonance. Our intensity measurements on the hot bands listed in Table II, show anomalies in the same sense as their findings. As seen, transitions from overtones of 01¹0 deviate progressively from the simple expectations.

Knowledge of harmonic frequencies and anharmonicity constants enables a calculation of zero-point energies, as it is given in the last line of Table III. It can be seen that the obtained values diminish in the sequence vapour — solution — liquid. It is remarkable that the magnitude of these shifts corresponds roughly to the level of van der Waals forces acting in a system packed as closely as the solution and the pure liquid. The shifts may be ascribed to interactions between vibrations and translations in the condensed phases.

In conclusion, it can be said that the three harmonic frequencies and seven anharmonicity constants, derived from the infrared and Raman spectrum of carbon disulphide in CCl₄, appear to take values which are between the ones obtained from the vapour-phase spectra and the ones from the pure liquid. The found exceptions of this regularity, the constants x_{22} , x_{12} and g_{22} , can be easily ascribed to their great sensitivity to errors made in frequency measurements. An overall characteristic of the condensed-phase constants is that five of them show a decrease compared to the vapor-phase constants (the ω 's, x_{13} and x_{23}), two increase (x_{11} and x_{12}), one is practically unchanged (x_{33}), while for one the sense cannot be determined with confidence (g_{22}).

In precise calculations, therefore, anharmonicity constants derived from gas—phase frequencies may not be sufficiently reliable.

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ИЗВОД

ВИБРАЦИОНА НЕХАРМОНИЧНОСТ НА МОЛЕКУЛИТЕ НА ЈАГЛЕН
ДИСУЛФИД ВО РАСТВОР*Б. Н. Шукарова и С. В. Рибникар*

Анализирани се инфрацрвените и раманските спектри на еднопроцентен раствор на јаглен дисулфид во јаглен тетрахлорид. Од десетте одбрани вибрациони премини определени се трите нулти фреквенции и седумте константи на нехармоничност. Споредување на овие константи со оние за CS_2 во гасовита и течна состојба покажува дека вредностите за растворот најчесто лежат помеѓу оние за гас и за течност. Тоа укажува на фактот дека при преминот од раствор кон течност нехармоничноста се изменува. Од друга страна, изгледа дека константата на фермиевската резонанца не се менува забележително при промена на состојбата.

ПРИРОДНО-МАТЕМАТИЧКИ ФАКУЛТЕТ
УНИВЕРЗИТЕТ ВО СКОПЈЕПримено на 20 декември 1974,
во изменета форма на 15 март 1975

и

ПРИРОДНО-МАТЕМАТИЧКИ ФАКУЛТЕТ
УНИВЕРЗИТЕТА У БЕОГРАДУ