INVESTIGATION OF ANTI-STOKES STIMULATED RAMAN SCATTERING ON MIXTURES OF BENZENE-CYCLOHEXANE

By

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The SRS spectra of mixtures of benzene — cyclohexane have been investigated. It has been shown that the spectra of mixtures can be interpreted on the basis of the combination principle with an error of ± 5 cm^{-1}. The number of spectrum lines showed a sharp maximum in case the mixture contained 20 per cent benzene and 80 per cent cyclohexane.

Only a few articles are known dealing with anti-Stokes stimulated Raman scattering (anti-Stokes SRS) of liquid mixtures [1—4]. In the present paper, to supply these lacks, we studied the anti-Stokes SRS spectra of cyclohexane, the mixture of benzene-cyclohexane and that of benzene. The latter deserves attention because while the spectrum of anti-Stokes SRS can be generally derived from a single line, this was not experienced at the cyclohexane. The behaviour of benzene-cyclohexane mixture is also strange because its anti-Stokes SRS spectrum contains a number of spectrum lines which are present neither in the anti-Stokes SRS spectrum of benzene nor in that of cyclohexane. Our aim was to investigate this effect on the basis of combinational principle.

Experimental arrangement

The anti-Stokes SRS spectra of the examined mixtures have been recorded by means of experimental appliance shown in Fig. 1. The Q-switching of the ruby laser was realized by vanadium-phtalocyanide solved in nitrobenzene. The diameter and the length of the ruby rod were 1.5 cm and 15 cm, respectively. The ruby laser worked in multi mode operation, the mean energy of the pulses were (1 ± 0.1) J, their duration about 30 ns, while the divergence of the laser beam was 7 mrad.

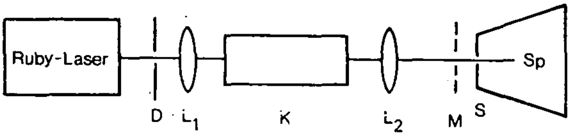

Fig. 1. Experimental appliance

A beam of round cross section was separated from the light of the ruby laser by means of the D diaphragm and it was focused with the help of a 5 cm focal length L_1 lens into the K cell containing the material to be studied. The length of the K cell was

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20 cm. There was a matte glass plate before the entrance slit of the spectrograph *Sp* on which the radiation coming from the cell was focused by the L_2 lens with a focal length of 40 cm. The distance between the L_2 lens and the exit window of the *K* cell was between 40 and 45 cm depending on the refractivity index of the mixture, while the distance between the entrance slit and the exit window of the cell was 240 cm. The spectrograph, applied in our experiments, was a three-prism Steinhel type with an apperture of 1 : 10. Its reciprocal linear dispersion was 4.5 nm/mm measured at wavelength of $\lambda=694.3$ nm and 0.947 nm/mm at that of $\lambda_{Cd}=467.186$ nm. The spectra was recorded on ORWO (Volfen) plane films type NP20, size of 9×12 cm^2. The range of the recorded spectra was between 800 and 470 nm. In general only a few spectrum lines were observable on the Stokes-side due to the low sensitivity of type NP20 film in the red spectral range. The exposed films were developed immediately after the expositions. A spectrum of a Hg—Cd lamp was recorded on each film. The prepared films were evaluated with the help of an ABBE-3-type comparator.

Description of anti-Stokes SRS spectra of mixtures

The classical description of Raman scattering interprets this effect as a scattering of light waves an optical phonons. The characteristics of the scattered radiation can be derived from the solution of a coupled system of partial differential equations. The solution of BLOEMBERGEN and SHEN [5] gives an account of the origin and direction -characteristic of first order Stokes and anti-Stokes radiation, respectively.

If the intensity of the exciting laser radiation is high enough, then the intensity of the developing first order Stokes radiation can reach the threshold intensity required to bring about the second order SRS and in a similar way develops the second order SRS.

Let us denote with $\bar{\nu}_m$ the wave number belonging to the single vibration state of the scattering homogeneous material, with $\bar{\nu}_L$ that of the exciting laser radiation. Then the wave number of the developing Stokes and anti-Stokes radiation is:

$$\bar{\nu}_{\mathrm{scatt}} = \bar{\nu}_L + n\bar{\nu}_m,$$

where $n=\pm1, \pm2, \ldots$ etc. can be.

If more molecule vibration $(\bar{\nu}_{m1}, \bar{\nu}_{m2}, \ldots, \bar{\nu}_{mk})$ can also occur simultaneously in the scattering material, then it can develop scattered radiation with the following wave numbers

$$\bar{\nu}_{\mathrm{scatt}} = \bar{\nu}_L + n_1\bar{\nu}_{m1} + n_2\bar{\nu}_{m2} + \ldots + n_k\bar{\nu}_{mk},$$

where each n_j is a positive and negative integer, or zero and its values are limited by the intensity ratios.

Experimental results

a) *The anti-Stokes SRS spectrum of benzene*

The stimulated Raman spectrum of the benzene on the anti-Stokes side contains the lines below according to our measurements [6] (see Table I).

Table I

$\Delta\bar{\nu}_{\text{meas.}}$ (cm^{-1})	0	991	1985	2974	3965
$\Delta\bar{\nu}_{\text{calc.}}$ (cm^{-1})	0	991	1982	2973	3964

In Table I $\Delta\bar{\nu}=\bar{\nu}_{\text{scatt}}-\bar{\nu}_L$. The mean error of measured wave number data are ± 2 cm^{-1}.

Similarly to most of the pure materials the Raman spectrum of benzene can derive from a single molecule vibration.

b) *The anti-Stokes SRS spectrum of cyclohexane*

Measurement results in the wave number shift of the individual spectrum lines are represented in Table II. Since the theoretical derivation of the obtained spectrum, containing 13 lines could mean the solution of coupled differential equations including $26+1=27$ equations, therefore the question has been put in the following way: How can the measured spectrum be regained by means of the combination formula, supposing the fewest possible independent spectrum lines?

The above spectrum can be given, based on the combination principle, with the following lines (see Table II):

Table II

n_2	n_3	n_4	$\Delta\bar{\nu}_{\text{calc.}}$ (cm^{-1})	$\Delta\bar{\nu}_{\text{meas.}}$ (cm^{-1})
1	0	0	—	799
0	1	0	—	1352
0	0	1	—	2856
−2	0	1	1258	1251
0	−1	1	1504	1506
2	0	0	1598	1605
−1	0	1	2057	2050
1	−1	1	2303	2308
1	0	1	3655	3656
−2	0	2	4114	4112
0	−1	2	4360	4366
−1	0	2	4913	4912
0	0	2	5712	5707

$$\Delta\bar{\nu}_{m2} = 799\ \text{cm}^{-1}, \quad \Delta\bar{\nu}_{m3} = 1352\ \text{cm}^{-1}, \quad \Delta\bar{\nu}_{m4} = 2856\ \text{cm}^{-1}.$$

For comparison the following spectrum lines can be found in the Raman spectrum of cyclohexane [6]

$$\Delta\bar{\nu}_{m2} = 800\ \text{cm}^{-1}, \quad \Delta\bar{\nu}_{m3} = 1350\ \text{cm}^{-1}, \quad \Delta\bar{\nu}_{m4} = 2858\ \text{cm}^{-1}.$$

c) *The anti-Stokes SRS spectrum of the benzene-cyclohexane mixture*

In our investigations the benzene concentration in the mixture was the following: 90, 80, ..., 20, 10 per cent. In the course of these measurements for high concentration of benzene (90—70 per cent) only the benzene lines appeared repeatedly. The line with wave number shift $\Delta\bar{\nu}=1352$ cm^{-1} also appeared at one or two occasions, and the combination of this line with a benzene line appeared too ($\Delta\bar{\nu}=1632\ \text{cm}^{-1}$). The higher the concentration of cyclohexane in the mixture, became the more lines appeared which can be found neither in the spectrum of the benzene nor in that of the cyclohexane.

Most of the lines appeared in the mixture containing 20 per cent benzene and 80 per cent cyclohexane. Altogether 60 lines were observed.

In order to describe the observed lines on the basis of the combination principle, all the possible combinations of the four independent lines so far described were calculated with the following restrictions

$$|n_1|_{\max} = 4, \quad |n_2|_{\max} = 2, \quad |n_3|_{\max} = 1, \quad |n_4|_{\max} = 2.$$

This means altogether 338 anti-Stokes lines. The wave number shift of all the lines we observed was in a good agreement with one of the possible 338 lines and almost in every case only with one of them. Merely 6—8 cases were to be questioned, when two calculated values were close to one measured value. In such cases that decided in favour of one combination where the absolute values of the combination coefficients involved were smaller than in the other combination. *E.g.* the combination coefficients (0, 0 —1, 1) give a wave number shift $\Delta\bar{\nu}=1504\ \text{cm}^{-1}$, the coefficients $(-4, -2, 1, 2)$ give a shift $\Delta\bar{\nu}=1502\ \text{cm}^{-1}$. Of the two shifts the former has obviously greater probability, while it is realized through less steps, and so it can be realized with an excitation of lower intensity than the latter shift.

Table III. below shows the results of calculations and measurements.

In Fig. 2 the anti-Stokes SRS spectra of the benzene, the mixture of 20 per cent benzene — 80 per cent cyclohexane and the pure cyclohexane can be seen.

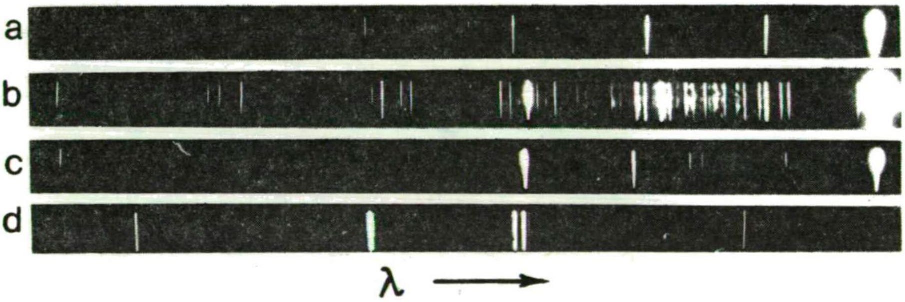

Fig. 2. The anti-Stokes SRS spectra of the benzene — *a*, the mixture of 20 per cent benzene — 80 per cent cyclohexane — *b* and the pure cyclohexane — *c*. The spectrum of a Hg—Cd lamp — *d*

Summary

On the course of the investigations the performed measurements concerning the anti-Stokes SRS spectrum of mixtures of benzene-cyclohexane have resulted plenty of lines. The interpretation of the spectrum can be given with the help of the combination principle with an error of ±5 cm⁻¹. The number of lines is dependent on the concentration and the maximum appears if the mixture contains 20 per cent benzene and 80 per cent cyclohexane. This can be used to produce a Raman-laser operating on discrete wavelengths.

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Table III

n_1	n_2	n_3	n_4	$\Delta\bar{\nu}_{\text{meas.}}$ (cm^{-1})	$\Delta\bar{\nu}_{\text{calc.}}$ (cm^{-1})	n_1	n_2	n_3	n_4	$\Delta\bar{\nu}_{\text{meas.}}$ (cm^{-1})	$\Delta\bar{\nu}_{\text{calc.}}$ (cm^{-1})
1	0	0	0	991	—	2	0	0	0	1985	1982
0	1	0	0	799	—	0	−1	0	1	2050	2057
0	0	1	0	1352	—	0	1	−1	1	2300	2303
0	0	0	1	2856	—	1	0	1	0	2335	2343
						4	−2	0	0	2367	2366
1	−1	0	0	190	192	−2	0	−1	2	2399	2378
−1	0	1	0	352	361	−1	−1	1	1	2405	2418
−1	2	0	0	603	607	3	1	−1	0	2429	2420
3	−1	1	−1	667	670	4	0	1	−1	2468	2460
−2	0	0	1	865	874	1	0	−1	1	2498	2495
3	1	0	−1	926	916	2	−1	1	0	2531	2535
−1	−1	0	1	1058	1066	1	2	0	0	2599	2589
4	0	0	−1	1116	1108	−1	1	0	1	2664	2664
2	−1	0	0	1184	1183	3	−2	1	0	2727	2727
0	−2	0	1	1251	1258	2	1	0	0	2782	2781
−1	1	−1	1	1306	1312	−2	−1	0	2	2919	2931
3	−2	0	0	1374	1375	0	2	1	0	2944	2950
2	1	−1	0	1442	1429	3	0	0	0	2974	2973
−3	2	0	1	1480	1481	1	−1	0	1	3045	3048
0	0	−1	1	1506	1504	0	2	−1	1	3111	3102
1	−1	1	0	1536	1544	0	1	0	1	3656	3655
−2	−1	−1	2	1573	1579	−2	0	0	2	3724	3730
0	2	0	0	1605	1598	1	0	0	1	3852	3847
3	0	−1	0	1632	1621	−1	−1	0	2	3914	3922
−2	1	0	1	1668	1673	2	−1	0	1	4044	4039
3	2	0	−1	1726	1715	0	0	−1	2	4366	4360
2	−2	1	0	1732	1736	−1	0	0	2	4721	4721
1	1	0	0	1792	1790	2	0	0	1	4845	4838
−1	0	0	1	1861	1865	0	−1	0	2	4912	4913
−3	−1	0	2	1924	1940	0	0	0	2	5707	5712

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ИССЛЕДОВАНИЕ АНТИСТОКСОВОГО ВЫНУЖДЕННОГО КОМБИНАЦИОННОГО РАССЕЯНИЯ СМЕСЕЙ ВЕНЗОЛА И ЦИКЛОГЕКСАНА

Ф. Пинтер, Л. Визе, Л. Гати, Т. Асталош

Нами были исследовани спектры ВКР смесей бензола и циклогексана. Показано, что спектры смесей обясняются на основе комбинационного принципа с точностю $\pm 5\,\text{см}^{-1}$. В случае состава смеси 20% бензола и 80% циклогексана, число спектральных линий показывает ярко выраженный максимум.