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ANHARMONICITY OF THE CARBON DIOXIDE MOLECULE IN SOLUTIONS OF ACETYLENE AND CARBON TETRACHLORIDE

by

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The anharmonicity of molecular vibrations is an essential factor determining the energy levels of the molecules. The question whether the degree of anharmonicity changes in the process of condensation has been checked recently on the example of carbon disulfide (1). No significant change was found. Another molecule of the same symmetry type, carbon dioxide, seemed appropriate to extend this investigation.

Since the recording of the infrared spectrum of liquid carbon dioxide presents a considerable technical problem (its triple point pressure being 5.2 atm), the closest approximation to this state was the recording of a carbon dioxide — acetylene mixture in a ratio 1 to 2. This system forms an eutectic mixture which melts at 170.3 K with a pressure of 0.32 atm (2), and hence could be safely handled with common cell windows. Another mixture was also recorded: a solution of carbon dioxide in carbon tetrachloride. Because of a rather low solubility, which is 1.07 mol per cent at one atmosphere and 25°C (3), some parts of the spectrum had to be recorded with solutions pressurized with carbon dioxide gas.

EXPERIMENTAL

Tank acetylene and tank carbon dioxide were passed through cold traps kept at dry ice — alcohol temperature, and mixed in a ratio 2 to 1. The mixture was condensed into a liquid which was distilled several times discarding first and last fractions. The same procedure was applied with acetylene-D_2, obtained from heavy water and calcium carbide.

Carbon tetrachloride was saturated with carbon dioxide either with a stream from sublimed dry ice prior to filling the cells, or with CO_2 gas applied as a static pressure above the solvent in an absorption cell designed to withstand increased pressures. The cell, used in the near infrared part of the spectrum, was made of a brass cylinder with glass windows 4 mm thick. The effective absorption length was 90 mm. It was operated up to 11 atm. Assuming the validity of Henry's law, this pressure would correspond to a concentration of about 11 mol per cent of CO_2 in carbon tetrachloride.

The recording of the infrared spectra at temperatures below ambient was made using a Variable Temperature Cell, Model VLT-2, of the I.C.I.C., London, following the filling procedure described in Ref. 4. The acetylene — carbon dioxide mixtures were kept at -80 ± 2°C using liquid nitrogen as coolant. Cell thicknesses were varied from 0.01 to 0.5 mm, using silver chloride windows.

The spectral range of 400 to 10,000 cm^{-1} was covered with spectrophotometers Perkin-Elmer 457, the UR-10 of Carl Zeiss, Jena, and the Beckman DK-1A. A Raman spectrum of the CCl_4-CO_2 solution was recorded with a Hilger & Watts Raman spectrometer with a 400 watt mercury arc excitation. Due to the faintness of the lines sought for, an extended photographic recording was done using the435.8 nm line for excitation.

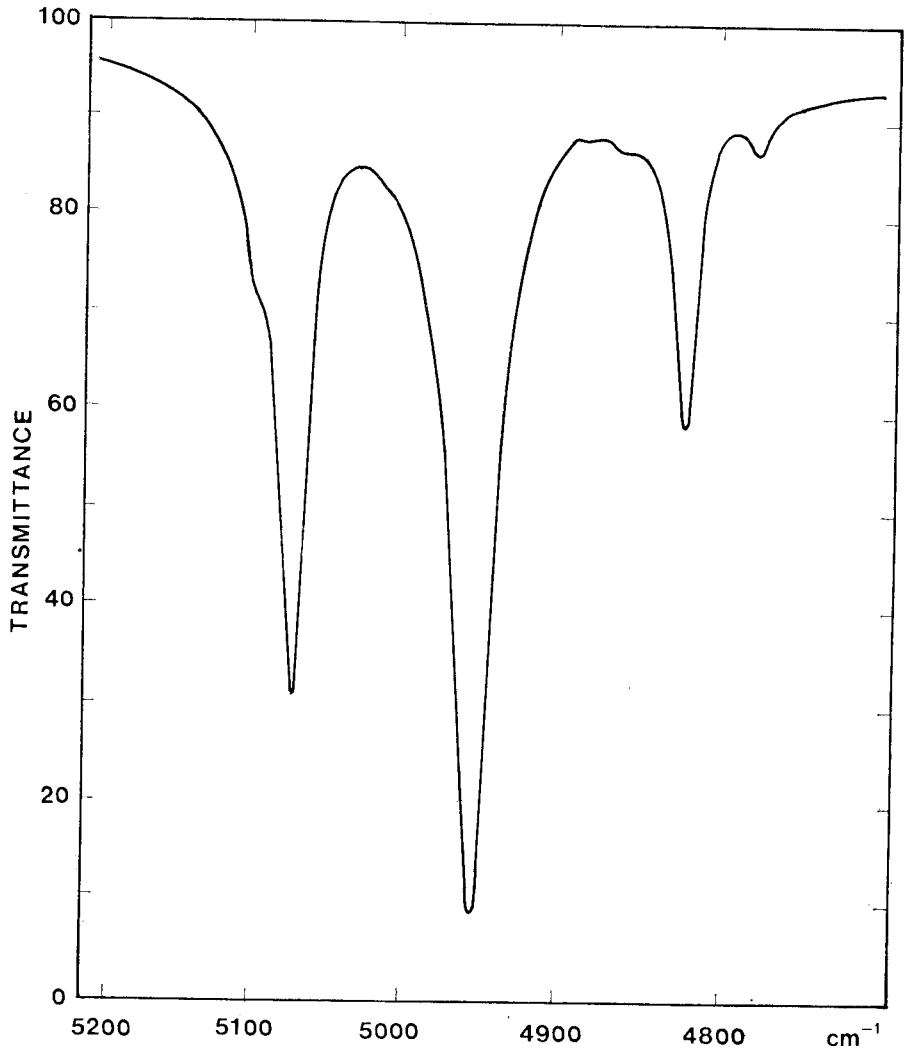

Fig. 1 — The first Σ-triad of carbon dioxide in CCl_4 solution. Concentration 9%, cell length 90 mm, 25°C.

Table 1 lists the measured carbon dioxide frequencies. A detail of the spectrum is shown in Fig. 1. The band positions of C_2H_2, C_2HD and C_2D_2 in the mixture are given in Table 2.

Nuclear magnetic resonance spectra of several liquid mixtures of acetylene and carbon dioxide were recorded at low temperatures with a Varian A 60 A NMR spectro-

TABLE 1

Vibrational frequencies of carbon dioxide dissolved in acetylene and carbon tetrachloride (cm^{-1}, vacuum corrected)

Transition[a]	Species	Gas[b]	$CO_2-C_2H_2$ −80°C	CO_2-CCl_4, 25°C		
				Obs.	Calcd.	Calcd.−Obs.
$01^10\leftarrow00^00$	$\Pi_u-\Sigma_g^+$	667.40	658	660	660	*
$02^00\leftarrow00^00$	$\Sigma_g^+-\Sigma_g^+$	1285.43	1278[c]	1276[c]	1276	*
$10^00\leftarrow00^00$	$\Sigma_g^+-\Sigma_g^+$	1388.15	1382	1379[d]	1379	*
$03^10\leftarrow00^00$	$\Pi_u-\Sigma_g^+$	1932.45	—	1917[e]	1916	−1
$11^10\leftarrow00^00$	$\Pi_u-\Sigma_g^+$	2076.85	—	—	2061	
$^{13}C00^01\leftarrow00^00$	$\Sigma_u^+-\Sigma_g^+$	2284.5	2278	2269		
$00^01\leftarrow00^00$	$\Sigma_u^+-\Sigma_g^+$	2349.16	2342.7[f]	2334.5	2334.5	*
$02^01\leftarrow00^00$	$\Sigma_u^+-\Sigma_g^+$	3612.79	3594	3590	3590	*
$10^01\leftarrow00^00$	$\Sigma_u^+-\Sigma_g^+$	3714.74	3700	3693	3693	*
$04^01\leftarrow00^00$	$\Sigma_u^+-\Sigma_g^+$	4853.56	4828	4824	4824	*
$12^01\leftarrow00^00$	$\Sigma_u^+-\Sigma_g^+$	4977.8	4959	4955	4955	*
$20^01\leftarrow00^00$	$\Sigma_u^+-\Sigma_g^+$	5099.63	5077[g]	5073	5073	*
$06^01\leftarrow00^00$	$\Sigma_u^+-\Sigma_g^+$	6075.97	—	—	6049	
$14^01\leftarrow00^00$	$\Sigma_u^+-\Sigma_g^+$	6227.92	—	6194[h]	6197	3
$22^01\leftarrow00^00$	$\Sigma_u^+-\Sigma_g^+$	6347.85	—	6319[h]	6319	0
$30^01\leftarrow00^00$	$\Sigma_u^+-\Sigma_g^+$	6503.09	—	—	6482	
$00^03\leftarrow00^00$	$\Sigma_u^+-\Sigma_g^+$	6972.49	—	6923[h]	6923	*
$02^00\leftarrow01^10$	$\Sigma_g^+-\Pi_u$	618.0	620	616	616	0
$10^00\leftarrow01^10$	$\Sigma_g^+-\Pi_u$	720.8	—	—	719	
$03^10\leftarrow02^00$	$\Pi_u-\Sigma_g^+$	647.02	—	641	640	−1
$11^10\leftarrow02^00$	$\Pi_u-\Sigma_g^+$	791.46	—	—	785	
$01^11\leftarrow01^10$	$\Pi_g-\Pi_u$	2336.68	—	2322	2322	0
$03^11\leftarrow01^10$	$\Pi_g-\Pi_u$	3580.27	—	3556	3558	2
$11^11\leftarrow01^10$	$\Pi_g-\Pi_u$	3723.19	—	3705	3702	−3
$05^11\leftarrow01^10$	$\Pi_g-\Pi_u$	4807.63	—	4780	4779	−1
$13^11\leftarrow01^10$	$\Pi_g-\Pi_u$	4965.35	—	—	4943	
$21^11\leftarrow01^10$	$\Pi_g-\Pi_u$	5123.17	—	5098	5099	1
$01^13\leftarrow01^10$	$\Pi_g-\Pi_u$	6935.07	—	6887[h]	6885	−2

a) Levels within braces are in Fermi resonance.
b) Ref. 8.
c) Calculated from difference bands 02^00-01^10.
d) Raman value.
e) Calculated from the difference band 03^10-02^00.
f) Because of too high intensity, the position was calculated from the ^{13}C band, assuming equal solution shifts in both systems.
g) Assumed by analogy with the same triad in CCl_4 solution.
h) Nine to eleven per cent solution. At least for the triad, there is no change within the scatter of data in the interval of 1 to 10 percent.

meter. The gases were mixed with tetramethyl silane internal standard, condensed into standard NMR tubes, sealed off, and transferred frozen to the precooled measuring compartment of the spectrometer. The recorded chemical shifts are presented in Table 3. In all the cases the acetylene proton peak was single and well defined.

In order to clarify some features appearing in the spectrum of the CCl_4 solution, a spectrum of dissolved $^{13}CO_2$ (8 per cent enrichment) was recorded in the region of the ν_3 band.

TABLE 2

Bands of acetylene, acetylene-D and acetylene-D_2 appearing in the liquid mixture with carbon dioxide at $-80°C$ (cm^{-1}).

Assignment	C_2H_2	C_2HD	C_2D_2
ν_5	755 v.s.*	697 s.	550 v.s.
$\nu_4+\nu_5$	1365 s.		1066 s.
$2\nu_4+\nu_5$	1962 m.		
ν_2		1840 m.	
$\nu_2+\nu_5$	2707 w.		
ν_3	3253 v.s.	2559 s.	2414 v.s.
ν_1		3304 s.	
$\nu_3+\nu_4$	3873 m.		2930 w.
$\nu_1+\nu_5$	4084 m.		

* v. — very, s. — strong, m. — medium, w. — weak.

The same region, with normal CO_2, was also recorded in chloroform and toluene as solvents. The cell temperature was varied from 25° to −62° and −76°C respectively. The relative intensities of two shoulders appearing on both sides of the ν_3 band were measured. The high frequency shoulder, shifted by 7 to 8 cm^{-1} from the band center,

TABLE 3

NMR chemical shifts of liquid acetylene and mixtures of acetylene and carbon dioxide (ppm against TMS).

Substance	Temperature, °C				
	−20	−30	−40	−50	−60
Liquid C_2H_2		2.00	2.03	2.05	2.07
$3C_2H_2+CO_2$	1.96	2.00		2.03	
$2C_2H_2+CO_2$		1.98	2.00	2.03	

stayed in the whole temperature interval in both solvents between 2 and 3 percent of the main band. The low frequency shoulder, after subtracting it from the whole, appears as a band with a maximum displaced by 11 to 12 cm^{-1}, with a wing extending towards lower frequencies. The contribution of this shoulder amounts to 16 percent of the whole

at 25°C. It decreases to 9 percent at the lowest temperatures. During these recordings the instrument was being constantly flushed with nitrogen. It should be noted that both shoulders, with practically equal displacements, appear in the ^{13}C peak, making thus an influence of possible impurities highly improbable.

Some of the CO_2 bands in solution have convenient frequency calibration points in their vicinity. The bands of ν_2 and ν_3 could be recorded with superimposed rotational lines of the corresponding CO_2 bands of the atmosphere (5–7). These recorded frequencies are therefore believed to be accurate within one wavenumber. The frequencies of the diad $02^{\circ}1/10^{\circ}1$ could be conveniently checked against the rotational structure of the atmospheric water band in their vicinity (5), giving again frequencies quite precisely known. The positions of the members of the triad $04^{\circ}1/12^{\circ}1/20^{\circ}1$ are determined less precisely and are believed to be accurate to 3 cm^{-1}. (The third member of this triad in C_2H_2 solution was for instrumental reasons not recorded and was given a frequency assumed by analogy with the other system; an error limit of ± 8 cm^{-1} is ascribed to it). The fundamental ν_1 appears quite weakly and broadly in the spectrum of the $C_2D_2-CO_2$ mixture 0.5 mm thick. In the CCl_4 solution it is hardly noticeable, but the Raman spectrum yielded a measurable band. A possible uncertainty of ± 3 cm^{-1} is ascribed to these data. For the other component of the first diad, $2\nu_2$, appearing poorly defined in both IR spectra, the frequencies accepted are from the difference bands $02^{\circ}0 \leftarrow 01^{1}0$, which are visible in the spectra of both systems. A possible error of ± 4 cm^{-1} is ascribed to these data. All these errors increase somewhat in the cases where Fermi resonance is involved, when corresponding unperturbed frequencies are calculated.

EVALUATION OF THE ANHARMONICITY CONSTANTS

In order to determine the three zero-order frequencies, ω_i, and the seven anharmonicity constants x_{ik} $(k \geqslant i)$ and g_{22}, a procedure similar to the one described in Ref. 1 was used. The first assumption taken was the equality of the quantum mechanical interaction constant, W, between the gaseous and dissolved states. For the resonance of levels with quantum numbers v_1, v_2, v_3, l_2 with levels (v_1-1), (v_2+2), v_3, l_2, the value of the interaction constant was calculated from the equation derived by Courtoy (8) for gaseous carbon dioxide:

$$W^2=(51.31-0.15\,v_1-0.41\,v_2-0.78\,v_3)^2\times\frac{1}{4}\,[(v_2^2+2)^2-l_2^2]\,v_1. \qquad (1)$$

The frequencies belonging to the levels perturbed by Fermi resonance were treated and the appropriate unperturbed frequencies calculated. The chosen ten frequencies are marked with asterisks in Table 1. The calculation of the positions of unperturbed levels of resonating diads is straightforward (9a), but in the case of the Σ-triad, an iterative procedure had to be used.

A set of ten equations with ten unknowns of the type

$$G_0\,(v_1, v_2, v_3, l_2)=\sum_i \omega_i\,v_i+\sum_i\sum_{k\geqslant i} x_{ik}\left(v_i\,v_k+\frac{v_i\,d_k}{2}+\frac{v_k\,d_i}{2}\right)+\sum_i\sum_{k\geqslant i} g_{ik}\,l_i\,l_k$$

is obtained, where G_0 is the unperturbed frequency and d_i and d_k are the degeneracies of the i-th and k-th levels. The augmented matrix of the system of equations for CO_2 in the CCl_4 solution is:

660.0	0	1	0	0	3	0	$\frac{1}{2}$	0	$\frac{1}{2}$	1
1321.8	0	2	0	0	8	0	1	0	1	0
1333.2	1	0	0	2	0	0	1	$\frac{1}{2}$	0	0
2334.5	0	0	1	0	0	2	0	$\frac{1}{2}$	1	0
3630.8	0	2	1	0	8	2	1	$\frac{1}{2}$	4	0
3652.2	1	0	1	2	0	2	1	2	1	0
4922.5	0	4	1	0	24	2	2	$\frac{1}{2}$	7	0
4957.9	1	2	1	2	8	2	4	2	4	0
4971.6	2	0	1	6	0	2	2	$\frac{7}{2}$	1	0
6923.0	0	0	3	0	0	12	0	$\frac{3}{2}$	3	0

where the columns correspond to G_0 and the coefficients of ω_1, ω_2, ω_3, x_1 x_{22}, x_{33}, x_{12}, x_{13}, x_{23} and g_{22}. The system can be solved with the aid of a electronic computer, but it can be shown that the solutions can also b obtained from the following relations:

$$x_{11}=\frac{1}{2}\,[(20^{\circ}1)_0-2\,(10^{\circ}1)_0+(00^{\circ}1)], \tag{2}$$

$$x_{22}=\frac{1}{8}\,[(04^{\circ}1)_0-2\,(02^{\circ}1)_0+(00^{\circ}1)], \tag{3}$$

$$x_{33}=\frac{1}{6}\,[(00^{\circ}3)-3\,(00^{\circ}1)], \tag{4}$$

$$x_{12}=\frac{1}{2}\,[(12^{\circ}1)_0-(10^{\circ}1)_0-(02^{\circ}1)_0+(00^{\circ}1)], \tag{5}$$

$$x_{13}=(10^{\circ}1)_0-(10^{\circ}1)_0-(00^{\circ}1), \tag{6}$$

$$x_{23}=\frac{1}{2}\,[(02^{\circ}1)_0-(02^{\circ}0)_0-(00^{\circ}1)], \tag{7}$$

$$g_{22}=\frac{1}{2}\,[2\,(01^{1}0)-(02^{\circ}0)_0+2\,x_{22}], \tag{8}$$

$$\omega_1 = 2\,(10^\circ 1)_0 + \frac{3}{2}\,(10^\circ 0)_0 - (20^\circ 1)_0 - (00^\circ 1) - \frac{1}{2}\,(12^\circ 1)_0 + \frac{1}{2}\,(02^\circ 1)_0, \tag{9}$$

$$\omega_2 = (02^\circ 1)_0 + \frac{3}{4}\,(02^\circ 0)_0 - \frac{1}{2}\,(00^\circ 1) - \frac{1}{2}\,(04^\circ 1)_0 - \frac{1}{4}\,(12^\circ 1)_0 + \frac{1}{4}\,(10^\circ 1)_0, \tag{10}$$

$$\omega_3 = 3\,(00^\circ 1) - \frac{1}{3}\,(00^\circ 3) - \frac{1}{2}\,[(10^\circ 1) + (02^\circ 1)] + \frac{1}{2}\,[(02^\circ 0) + (10^\circ 0)], \tag{11}$$

where $(v_1\, v_2^l\, v_3)$ aer the observed (unperturbed) frequencies, while the terms indexed zero represent the unperturbed energies calculated in the previously mentioned manner. It should be noted that the solutions for x_{33} and ω_3 can be obtained without knowing the resonance parameters, i.e. only unperturbed terms and sums of resonating ones are involved.

The solution was complete for the carbon tetrachloride solution, but in the acetylene system two frequencies were missing: 20°1 and 00°3. The former one was assumed, as said, by analogy. Instead of the latter, which is necessary to compute x_{33}, the value of this constant was assumed to be the same in both sets. The results of the calculation are given in Table 4. The error limits attached originate only from the estimated uncertainties in frequency determination.

TABLE 4

Anharmonicity constants of gaseous and dissolved carbon dioxide (cm^{-1})

Constant	Gas		CO_2 in C_2H_2 −80°C	CO_2 in CCl_4 25°C
	Ref. 9b	Ref. 8		
ω_1	1351.2	1354.94	1352.0±12	1334.7±10
ω_2	672.2	673.02	661.8±6	667.3±4
ω_3	2396.4	2396.40	2395.2±7	2381.8±5
x_{11}	−0.3	−3.75	−4.3±4	0.8±3
x_{22}	−1.3	−0.63	1.0±1	−0.6±1
x_{33}	−12.5	−12.63	(−13.4)	−13.4±3
x_{12}	5.7	3.62	5.2±6	4.7±4
x_{13}	−21.9	−19.37	−18.6±6	−15.5±5
x_{23}	−11.0	−12.53	−16.4±3	−12.7±2
g_{22}	1.7	0.775	−1.3±3	−1.5±3

For the set of constants of the CCl_4 solution, in the case of the constant x_{23}, besides Eq. 7, two additional checks are available. It can be shown that the difference in frequency between the transition $00^\circ 1 \leftarrow 00^\circ 0$ and its "hot" band $01^{1}1 \leftarrow 01^{1}0$ equals $-x_{23}$, while analogously the difference between $00^\circ 3 \leftarrow 00^\circ 0$ and $01^{1}3 \leftarrow 01^{1}0$ equals $-3\,x_{23}$. The Eq. 7 value is $-12.7 \pm \pm 2\ cm^{-1}$, while the other two methods yield -11.5 ± 1 and -12.4 ± 0.6 respectively. The agreement is quite satisfactory.

Unperturbed frequencies for all levels can be calculated now and appropriate perturbation calculation applied. Triads were treated according to Kovács and Singer (10) and the tetrad according to Brandt (11), taking Eq. 1 into account.

The calculated frequencies are listed in Column 6 of Table 1. This applies only to the CCl_4 solution data since all the observed frequencies in the acetylene solution were involved in the calculation, and the obtained values are predetermined to agree fully.

DISCUSSION

Two transitions have been detected in the infrared which are normally forbidden by the rule of mutual exclusion: the band of ν_1 in both solutions and the band of $2\nu_2$ in the acetylene solution. This is by no means surprising in view of the fact that both bands appear even in pressurized CO_2 gas (12) and the same behavior could be expected by analogy with carbon disulfide in liquid and dissolved states (1). Increased dilution tends to diminish their intensity (1, 13), which explains the findings in the CCl_4 solution.

The room temperature spectrum of the CCl_4 solution contains a multitude of difference and "hot" bands which are missing in the low temperature spectrum of the acetylene solution. This is to be expected because of a considerably smaller population of levels where these transitions originate.

One of the "hot" bands is the transition $01^11 \leftarrow 01^10$ accompanying the band of ν_3. It appears as a shoulder on the low frequency side of the main band. It has been noticed also by Cunliffe-Jones (14) in solutions of CO_2 in CCl_4 and various other solvents. The relative intensity of this band does not, however, agree with the one predicted from the population of the doubly degenerate level 01^10. Instead of 8.4 per cent, its intensity amounts to 16 per cent. On cooling to some $-70°C$ the population of the level 01^10 is expected to decrease to 1.6 per cent, i.e. a 6.8 point change. The found decrease from 16 to 9 per cent is also a 7 per cent change, pointing to a temperature independent component of this shoulder. No conceivable transition could be found to explain the origin of this band, as well as the one on the high frequency side. It is known, however, that some small molecules, like CO, NO and CH_4, retain some of their rotational energy in solutions, producing in their spectra wings on absorption bands, which are remnants of their *P*- and *R*-branches in the gas (15). These wings are in addition found to be almost temperature insensitive. Since the molecular diameter of CO_2, which is 3.8Å (Lennard-Jones potential), does not differ considerably from the diameters of the above mentioned molecules (3.7, 3.4 and 3.8Å respectively), it seems reasonable to assume some free rotation of carbon dioxide in the CCl_4 solution, and to ascribe the two observed side-bands to unresolved rotational structure.

The two CO_2 bands in the acetylene mixture, ν_1 and $2\nu_2$, appear to be closer to the ones in CCl_4 solution than to the ones found in the room temperature Raman spectrum of liquid CO_2 (16), although the difference of some 100 degrees between the temperatures of recording does not allow a definite conclusion. On the other hand, the virtual absence of influence of CO_2 on the acetylene proton resonance frequency, as found in the NMR spectrum, points to the absence of intermolecular interactions between CO_2 and C_2H_2 in their liquid mixtures. This fact might, firstly, mean that the

recorded spectrum resembles very much to the spectrum liquid acetylene would have at this temperature, and secondly, casts some light on the appearance of the deeply lying eutectic mixture formed by these two substances. Namely, both compounds show anomalously high triple points in their pure states. When mixed, their behavior approaches the one of "normal" substances. This might mean that the forces holding both CO_2 and C_2H_2 together in their solid states are a rather spatial effect, a consequence of packing, which disappears when these substances are mixed. The packing in the crystal, where the high site symmetry allows a strainless arrangement of the molecules, does not affect their symmetry, which can be concluded from the absence of "forbidden" bands in the crystal spectrum (17). In the cases of pressurized and dissolved CO_2, random interactions may produce a deformation of the molecules, changing their symmetry from $D_{\infty h}$ to C_s, similar to carbon disulfide (1). An alternate explanation might be given without assuming a molecular geometry change, considering only van der Waals interaction forces: the CO_2 molecules at the moment of a *close* collision, because of dispersion forces, or quadrupole-quadrupole interaction, may suffer an electrical asymmetry. Close collisions are most frequent in the liquid state. They are much less frequent in the gas, and in the solid the molecules are held at fixed distances by the crystal lattice.

As can be seen from Eqs. 2 to 11, the values of the anharmonicity constants are obtained as small differences between large numbers. They are affected therefore directly by the uncertainties in frequency determination. However, the agreement between the observed and calculated band frequencies seems to be quite satisfactory, since some errors obviously cancel each other. This agreement is comparable to the one found in the case of carbon disulfide (1), where the Fermi resonance plays a less significant role. It can be concluded that the application of the interaction constants found for gaseous CO_2 does not introduce serious deviations, at least not larger than the experimental error in the present determination.

The average (absolute) deviation between the calculated and observed values of the 11 bands not used in setting the system of constants, is about 0.1 per cent in the frequencies. Even if one assumes no change in the x's between the gas and solution, and corrects the gaseous zero-order frequencies just for the observed gas — solution frequency shifts of the fundamentals, the agreement is 0.2 percent on the average. This should be compared with the situation where no anharmonicity and resonance is taken into account, when the average error exceeds 2 percent.

CONCLUSIONS

1. Recorded infrared and Raman frequencies of carbon dioxide dissolved in CCl_4 at room temperature, or as a liquid mixture with acetylene at $-80°C$, can be used to obtain the anharmonicity constants and zero-order frequencies of the molecule.

2. The obtained anharmonicity constants do not differ substantially from the ones derived from the gas spectra. The differences are expressed in the change of the zero-order frequencies.

3. The band frequencies calculated using these constants, and the Ferm resonance interaction constants derived from the gas spectra, yield a satisfactory agreement within the limits of experimental errors.

4. Appearance of infrared "forbidden" bands in the solution spectra means either that tha CO_2 molecule suffered a deformation in the solution or that random close collisions have induced electrical asymmetry.

5. Remnants of gaseous *P*- and *R*-branches could be detected on the sides of the band of ν_3 in the CCl_4 solution, indicating some free rotation in the solution.

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SUMMARY

The infrared spectra of a liquid mixture of carbon dioxide and acetylene (1:2) at −80°C were recorded in the interval 400 to 5000 cm^{-1}. Infrared and Raman spectra of solutions of CO_2 in CCl_4 were recorded up to 10,000 cm^{-1}. From the found band frequencies, the anharmonicity constants and the zero-order frequencies of the CO_2 molecule were calculated for both systems. It was found that dissolution does not measurably affect the anharmonicity constants; the difference is expressed in the zero-order frequencies. The agreement between the positions of calculated and found bands is 0.1 percent on the average.

The ν_3 band of CO_2 in CCl_4 exhibits two weaker and temperature independent side-bands. They have been explained as remnants of the rotational branches of the gas spectrum, indicating a certain degree of free rotation of CO_2 in this solution.

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ИЗВОД

НЕХАРМОНИЧНОСТ МОЛЕКУЛА КАРБОН-ДИОКСИДА У РАСТВОРИМА У АЦЕТИЛЕНУ И КАРБОН-ТЕТРАХЛОРИДУ

ОД

СЛОБОДАНА В. РИБНИКАРА, ОЛГЕ С. ПУЗИЋ и БИЉАНЕ Н. ШУКАРОВЕ

Снимљени су инфрацрвени спектри течне смеше карбон-диоксида и ацетилена (1 : 2) на —80°C у интервалу од 400 до 5000 cm^{-1}. Такође су снимљени инфрацрвени и раманski спектри раствора карбон-диоксида у карбон-тетрахлориду до 10.000 cm^{-1}. Из нађених фреквенција трака израчунате су фреквенције нултог реда и седам константи нехармоничности молекула CO_2 за оба система. Нађено је да растварање битно не утиче на константе нехармоничности већ се манифестује у промени фреквенција нултог реда. Слагање измерених и израчунатих положаја трака је у просеку 0,1%.

Трака ν_3 карбон-диоксида у CCl_4 има два температурски непроменљива пратиоца мањег интензитета. Показано је да они представљају остатке грана P и R гасног спектра, што указује на известан степен слободне ротације молекула CO_2 у овом раствору.

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