

# RESONANCE RAMAN SPECTROSCOPIC STUDY ON IODINE IN VARIOUS ORGANIC SOLVENTS: SPECTROSCOPIC CONSTANTS AND HALFBAND WIDTHS OF THE I<sub>2</sub> VIBRATION\* \*\*

W. KIEFER†

*Sektion Physik der Universität München, Lehrstuhl J. Brandmüller,  
D-8 München 40, Germany*

and

H. J. BERNSTEIN

*Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada*

(Received 14 June, 1973)

**Abstract.** Resonance Raman spectra have been obtained from various iodine solutions. High intensity overtone progressions of the stretching vibration were observed, allowing the determination of the spectroscopy constants  $\omega_e$  and  $\omega_e x_e$  and an estimation of  $\omega_e y_e$  for the stretching vibration for the ground state in various environments. The values are compared to those obtained for the gas phase. The overtone progression shows a large increase in half-bandwidth with increasing vibrational quantum number.

## 1. Introduction

We have recently observed a remarkable fine structure in the overtone progression of the resonance Raman spectrum of iodine vapor with argon ion laser excitation [1, 2]. The observed resonance Raman spectrum (RRS) could be interpreted in terms of  $Q$  branches,  $S$  bandheads and vibrational hot band structure. The observation of many vibrational-rotational transitions in the resonance Raman effect (RRE) of iodine vapor made it possible to determine the spectroscopic constant  $\omega_e$ ,  $\omega_e x_e$  and  $\omega_e y_e$  with fairly high accuracy. Good agreement was achieved by comparing the data with those obtained from high resolution fluorescence measurements [3]. Since the latter method is not applicable for liquids we have attempted to derive the spectroscopic constants of iodine dissolved in a variety of solvents by carefully measuring the wavenumbers of the overtone progression. In this paper we present and discuss these measurements.

Usually excitation below the dissociation limit of the excited state of iodine yields a fluorescence spectrum rather than a resonance Raman spectrum [4]. In the liquid phase, however, the fluorescence is mostly quenched by the adjacent molecules of the solvent. If the quenching is efficient enough the RRS can be obtained. This was first observed by Beattie *et al.* [5] for iodine dissolved in cyclohexane and Mortensen [6] for an iodine/chloroform solution. Due to the lack of an efficient experimental

\* Issued as NRCC No. 13462.

\*\* Presented in part at the 26th Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, U.S.A., June 1971.

† NRCC Postdoctorate Fellow 1970-72.

arrangement only some of the lower overtones could be observed which consequently allowed only a rough estimation of the anharmonic constant  $\omega_e x_e$  [6]. We have shown [7] that rotation of the sample in front of the spectrometer increases the amount of collected Raman scattered photons by at least one order of magnitude. With this technique we were able to observe an overtone progression of the iodine vibration up to the 15th or in some cases even up to the 20th harmonic.

## 2. Experimental

The resonance Raman spectra were excited with the 5145 Å line of an argon ion laser (Coherent Radiation model 52). The power was about 1 W. In cases where the visible absorption spectrum of the iodine solution was shifted to lower wavelengths, the higher frequency laser lines (5017, 4965, 4880, 4765 and 4579 Å) were also used. The spectra were obtained with a Jarrell-Ash model 25-102 one meter double monochromator using a cooled ITT FW-130 photomultiplier and photon counting electronics. To avoid heating of the sample and a resulting thermal lens effect the rotating Raman sample technique [7] was employed. For wavenumber determinations neon, argon and xenon discharge lamps were used simultaneously during the recording of the Raman spectrum. The wavenumbers have been measured several times, some of the measurements were repeated with another Raman spectrometer in Munich. The accuracy of the reported band positions is therefore believed to be  $\pm 0.5 \text{ cm}^{-1}$  for sharp Raman lines. Broader bands may have an accuracy of only  $\pm 1$  to  $\pm 3 \text{ cm}^{-1}$  depending on the halfbandwidth of the line. The halfbandwidths were determined with spectral slit widths smaller than the observed bandwidth by a factor of about 4, so there is no large contribution of the slit function to the natural profile.

The solutions were prepared using iodine which was analytical reagent and spectrograde solvents without further purification. Concentrations of the order of  $10^{-2}$  mole  $\text{l}^{-1}$  were found to be most suitable for our studies.

The absorption spectra of the solutions were recorded with a Cary model 14 spectrophotometer.

## 3. Experimental Results and Discussion

### 3.1. THE OBSERVED RR SPECTRA OF VARIOUS IODINE SOLUTIONS

The electronic absorption spectra of the iodine solutions under investigation are shown in Figure 1. The relative positions of the visible laser lines of the argon ion laser are marked by vertical lines. From the positions of the maximum of the iodine absorption bands one can characterize three groups of solvents. Group I gives an absorption maximum around 5200 Å (carbonyl disulfide, cyclohexane, cyclopentane, *n*-pentane, *n*-hexane, *n*-heptane, carbontetrachloride and chloroform). Group II consists of *p*-xylene, toluene and benzene with maxima around 4950 Å, whereas iodine solutions in *p*-dioxane have a maximum at around 4500 Å. Therefore, if the laser line at 5145 Å is used for excitation, a strong RRE is to be expected for group I solutions [8], a weaker effect for group II and weaker still for *p*-dioxane. To illuminate

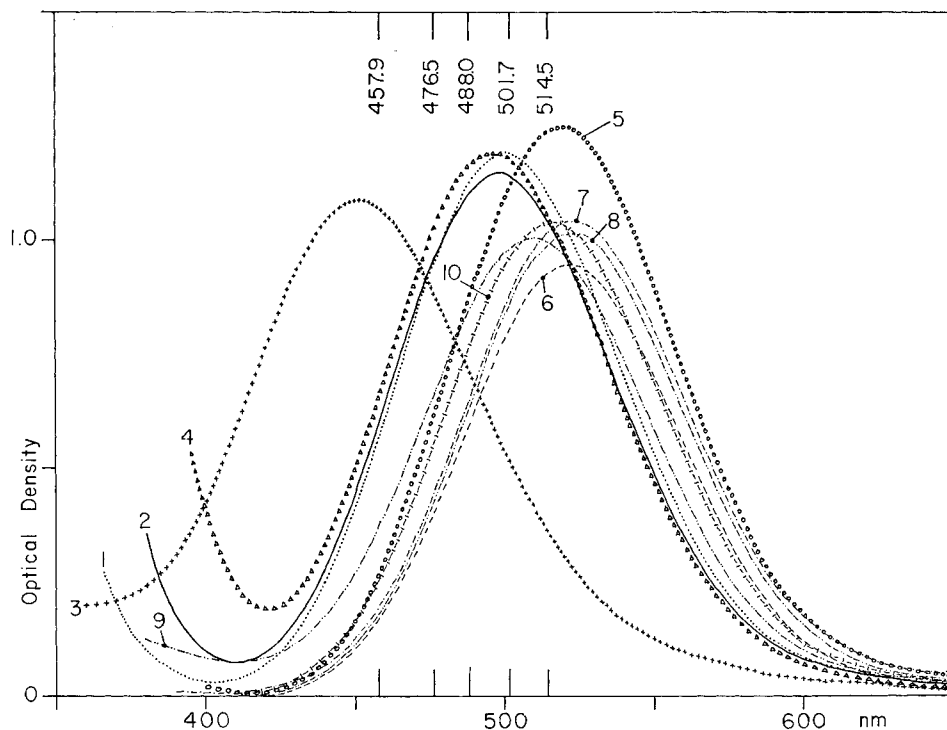


Fig. 1. Visible absorption spectra of various iodine solutions. Concentration  $10^{-2}$  mole  $l^{-1}$ . Path-length 0.1 cm. Solvents: (1) benzene, (2) toluene, (3) *p*-dioxane, (4) *p*-xylene, (5) carbondisulfide, (6) *n*-pentane, (7) cyclohexane, (8) cyclopentane or *n*-hexane, (9) chloroform, (10) carbontetrachloride.

the correlation between electronic absorption and RRE intensities a complete intensity study was carried out for this system (intensity of the fundamental as a function of exciting frequency as well as the intensity distribution within the overtone progression). This will be published in a following paper [9].

A large overtone progression for the group I solvents was achieved using 5145 Å excitation. Figures 2 to 4 show the RR spectra of iodine solutions at a concentration of  $10^{-2}$  mole  $l^{-1}$  for the solvents belonging to group I. The lines corresponding to the fundamental and the overtones of the  $I_2$  stretching vibration are marked by numbers which correspond to the change in vibrational quantum number. Table I collects the observed wavenumbers. The observed data of Mortensen [6] for the chloroform solution are also given.

Some of the RR lines of the progression coincide with Raman lines of the solvent. In these cases the wavenumbers were measured at highest possible resolution and the bands were deconvoluted to give more accurate values for the wavenumbers. If no appropriate deconvolution was possible the corresponding wavenumber for the iodine vibration was left out of Table I. The problem could have been solved more elegantly by using the recently developed difference Raman technique (divided rotating cell)

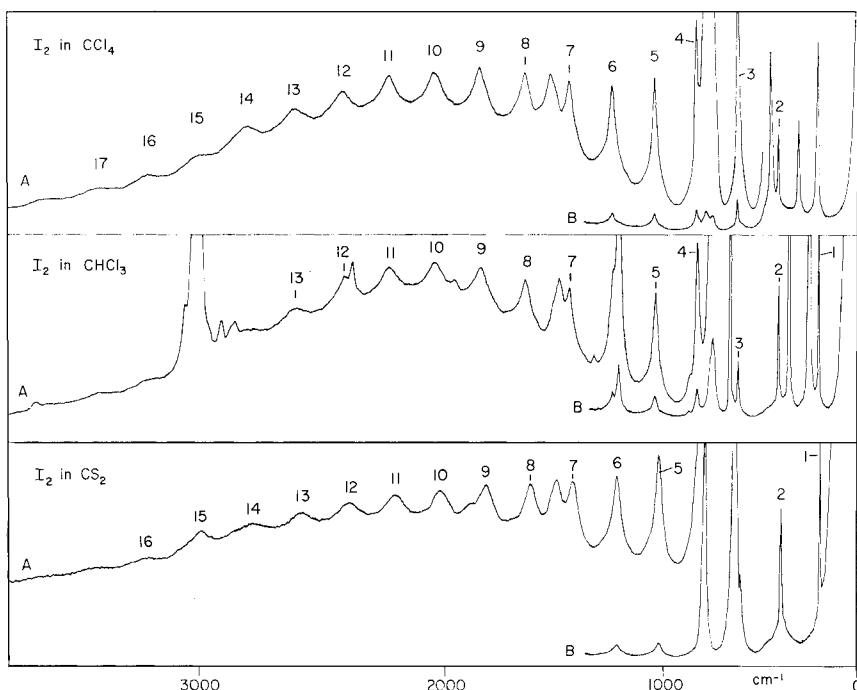


Fig. 2. Resonance Raman spectra of iodine in carbontetrachloride, chloroform and carbondisulfide. Concentration  $c = 10^{-2}$  mole  $l^{-1}$ ; excitation  $\lambda_0 = 5145 \text{ \AA}$ ; A: slits  $s = 300 \mu$  ( $\hat{=}$   $7.5 \text{ cm}^{-1}$  at  $3000 \text{ cm}^{-1}$ ), time constant  $t = 3 \text{ s}$ , speed  $v = 12.5 \text{ \AA min}^{-1}$ ; B:  $s = 100 \mu$  ( $\hat{=}$   $3 \text{ cm}^{-1}$  at  $750 \text{ cm}^{-1}$ ),  $t = 1 \text{ s}$ ,  $v = 12.5 \text{ \AA min}^{-1}$ .

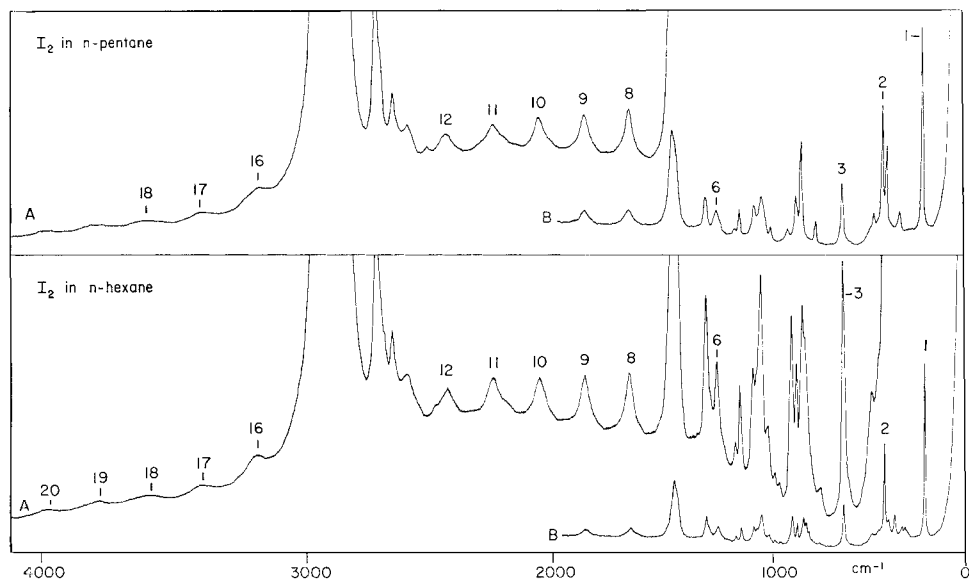


Fig. 3. Resonance Raman spectra of iodine in *n*-pentane and *n*-hexane. Caption as in Figure 2.

TABLE I  
Observed wavenumbers of the fundamental vibration and the overtone progression of iodine in various solvents (in cm<sup>-1</sup>)

Solvent	Vibrational quantum number														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Carbontetrachloride	211.4	421.4	630.3	837.6	1044.5	1249.4	1452.7	1655	1857.5	2055	2251.5	2449	2642	2829	3029
Chloroform	210.9	420.4	629.1	836.0	1041.1	-	1448.5	1648.5	1848.5	2046.5	2246	2438	2630	-	-
Chloroform <sup>a</sup>	211	420	626	832	1037	-	-	-	-	-	-	-	-	-	-
Carbondisulfide	207.0	412.7	-	-	1023.9	1227	1428	1628	1829	2025	2221	2418	2609	2801	2994
<i>n</i> -pentane	211.5	422.0	630.4	-	-	1252.1	-	1659	1860	2058	2254	2452	-	-	-
<i>n</i> -hexane	211.2	421.3	630.6	838.6	-	1250.5	-	1657	1858	2056	2252	2446	-	-	-
<i>n</i> -heptane	211.3	421.8	630.9	838.9	-	-	-	1657.5	1858	2055.5	2248	2447	-	-	-
Cyclopentane	211.4	421.8	630.9	838.1	-	-	-	1658	1858	2056	2250	2449	-	-	-
Cyclohexane	211.4	421.6	630.2	838.4	-	-	-	1655	1857	2054	2250	-	-	-	-
Benzene	205.2	407.9	-	810.7	-	-	-	-	-	-	-	-	-	-	-
Toluene	203.9	407.3	607.9	-	-	-	-	-	-	-	-	-	-	-	-
<i>p</i> -dioxane	203.8	406.6	-	-	-	-	-	-	-	-	-	-	-	-	-
<i>p</i> -xylene	203.3	404.6	604.7	-	-	-	-	-	-	-	-	-	-	-	-

<sup>a</sup> Reference 6.

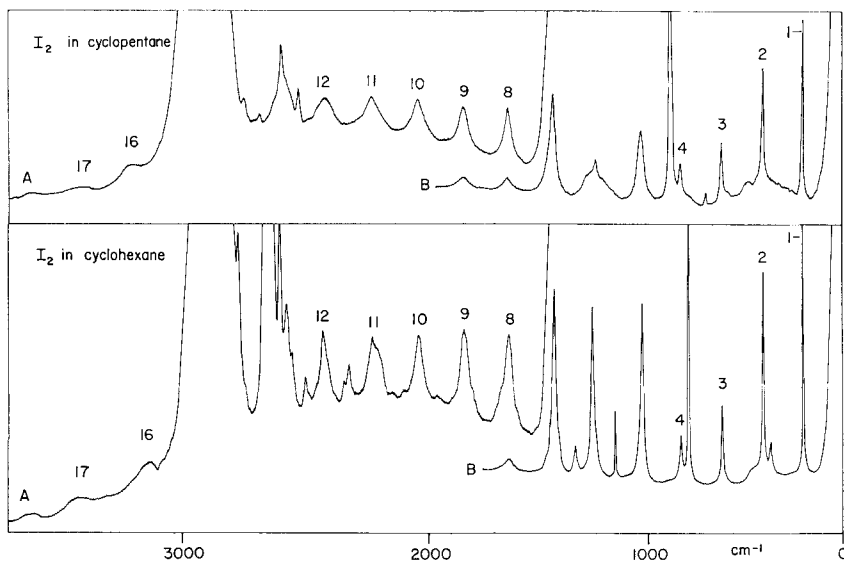


Fig. 4. Resonance Raman spectra of iodine in cyclopentane and cyclohexane. Caption as in Figure 2.

with which the Raman lines of the solvent can be cancelled [10]. However this equipment was not available at the time when these measurements were done.

As can be seen in Figures 2 to 4 the overtone progression decreases in intensity but increases in halfbandwidth with higher vibrational quantum number  $v$ . In all the spectra a high broadband background with maximum around  $2000\text{ cm}^{-1}$  was observed (see for instance the spectrum of the chloroform solution). This may be due to the fact, that the fluorescence quenching by the solvent molecules was not complete.

### 3.2. SPECTROSCOPIC CONSTANTS OF THE $I_2$ VIBRATION IN VARIOUS ORGANIC IODINE SOLUTIONS

The observation of high intensity overtone progressions in the RRE allows one to determine anharmonicity constants of particular vibrations. The observed wavenumbers  $\nu(v)$  of an anharmonic diatomic oscillator is given by [11]:

$$\begin{aligned} \nu(v) = G(v) - G(0) = v\omega_e - (v^2 + v)\omega_e x_e + \\ + (v^3 + 3/2v^2 + 3/4v)\omega_e y_e + \dots, \end{aligned} \quad (1)$$

where  $G(v)$  is the term value of the  $v$ th eigenvalue,  $v$  the vibrational quantum number,  $\omega_e$  is the harmonic frequency, and  $\omega_e x_e$  and  $\omega_e y_e$  the first and second anharmonicity constants. The spectroscopic constants of iodine in the gas phase and its electronic ground state have been recently derived by the authors using the wavenumbers of observed  $Q$  branches and  $S$  bandheads [1]. Here the spectroscopic temperature is very high due to the strong absorption [1]. Therefore a large contribution of the rotation of the iodine molecule to the overall bandshape of the overtones has to be taken

into account. In the liquid phase, however, the temperature of the sample is nearly room temperature, because the rotating sample technique [7] was employed. Since no thermal lens effect was observed, we conclude that little or no temperature increase took place. Moreover all observed overtones have a symmetrical band profile. Thus we make the assumption that to a great part, only the vibrational energy contributes to the observed band shape. The wavenumbers of the overtone progressions were therefore measured at the maxima of the observed band shape. The plots  $\nu_{\text{obs}}/\nu$  vs  $\nu$  of the group I solvents are displayed in Figures 5 to 8. We can see that the values corresponding to the lower vibrational quantum numbers are all located very closely on a straight line. The slope of this line gives the value for  $\omega_e x_e$ . For higher  $\nu$ , however, the influence of the second anharmonic constant is large enough to be detected. In all solutions

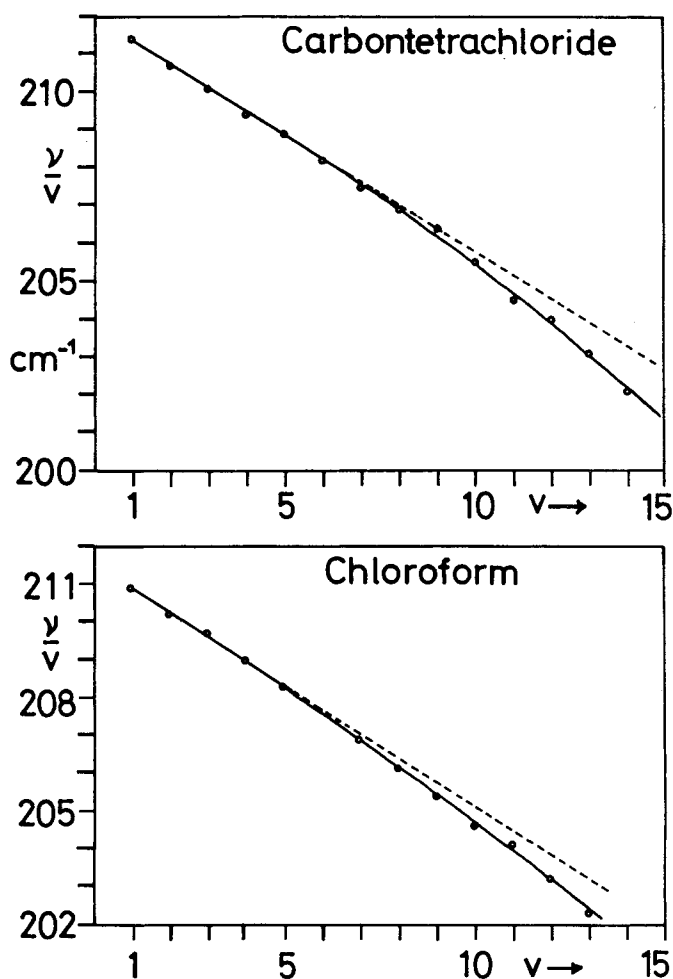


Fig. 5. Determination of anharmonic constants  $\omega_e x_e$  and  $\omega_e y_e$  of iodine in carbon tetrachloride and chloroform. A plot of  $\nu_{\text{observed}}/\nu$  vs the vibrational quantum number  $\nu$ .

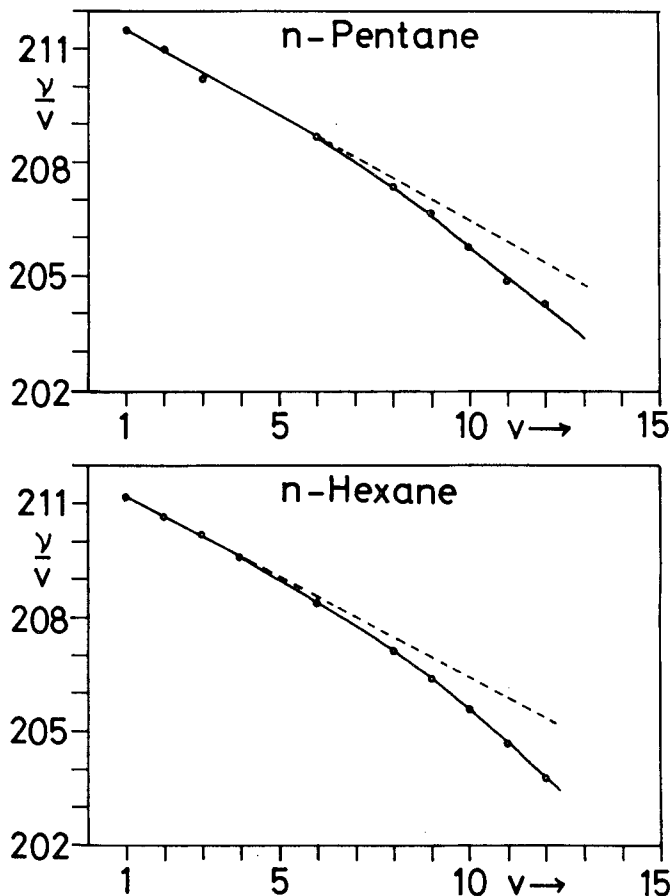


Fig. 6. Caption as in Figure 5, except for the solvents: *n*-pentane and *n*-hexane.

under investigation the  $\nu_{\text{obs}}/\nu$  values at higher vibrational quantum numbers are located significantly lower than those, calculated using only the first anharmonic constant. The deviation from the straight (dotted) line in Figures 5 to 8 allows one to determine the second anharmonicity constant  $\omega_e y_e$ . The harmonic frequency  $\omega_e$  can then be calculated using Equation (1), the derived values for  $\omega_e x_e$  and  $\omega_e y_e$  and the measured value of  $\nu(v)$ .

The values for the spectroscopic constants of the molecular iodine vibration in various solvents derived in the above mentioned way, are collected in Table II together with those obtained by Mortensen [6] for an iodine/chloroform solution. The gas phase data [1] are also presented.

If the interaction of the iodine molecule with the solvent molecule is small [12] the value for the harmonic frequency  $\omega_e$  is very close to the gas phase value of  $214.534 \text{ cm}^{-1}$ . This is the case for iodine dissolved in carbon tetrachloride, chloroform, *n*-pentane, *n*-hexane, *n*-heptane, cyclopentane and cyclohexane. When interaction



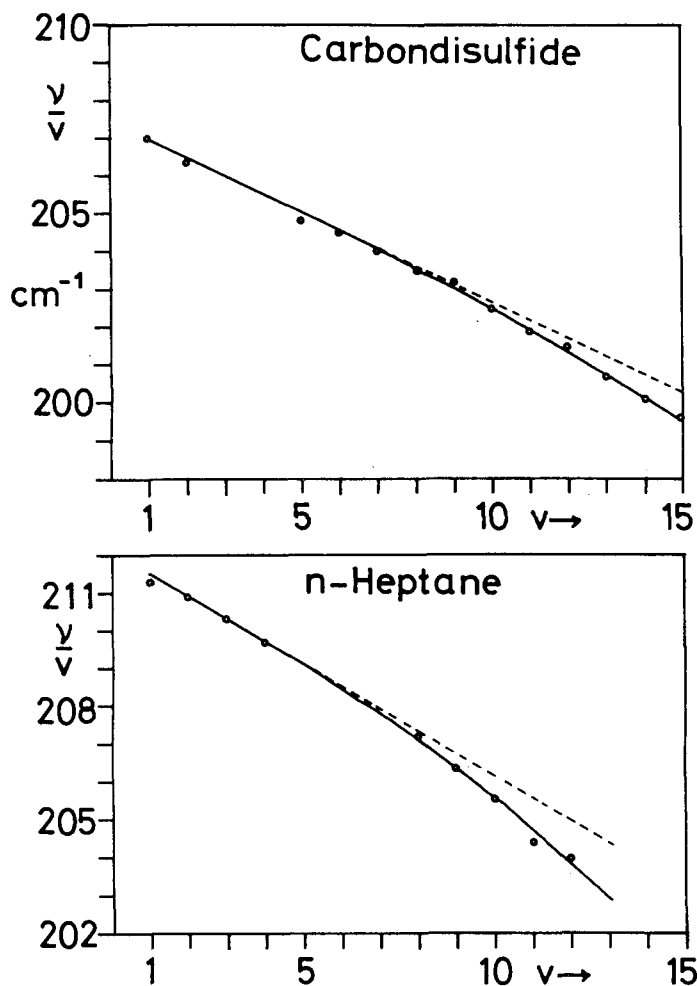


Fig. 7. Caption as in Figure 5 except for the solvents: carbondisulfide and *n*-heptane.

with the solvent is greater,  $\omega_e$  shifts to lower wavenumbers [12] (see also Table II,  $\omega_e$  for benzene, toluene, *p*-dioxane and *p*-xylene). The first anharmonic constant  $\omega_e x_e$  does not change appreciably within the experimental error for all solutions, except carbon disulfide, for which  $\omega_e x_e = 0.48 \pm 0.03 \text{ cm}^{-1}$  compared to the gas phase value of  $0.607 \pm 0.008 \text{ cm}^{-1}$  [1].

The data for the spectroscopic constants of iodine in solutions of benzene, toluene, *p*-xylene and *p*-dioxane are not as good as those obtained for the group I solvents, because in these cases overtone progressions only up to about the 4th harmonic could be observed with reasonable signal to noise ratios [9]. With more accurate data it is possible that changes in  $\omega_e x_e$  may be observed for  $\text{I}_2$  in these solvents.

The accuracy of the data for the second anharmonicity constant is – as expected – not very high (of the order of 50%), but we found that in all cases a large change in

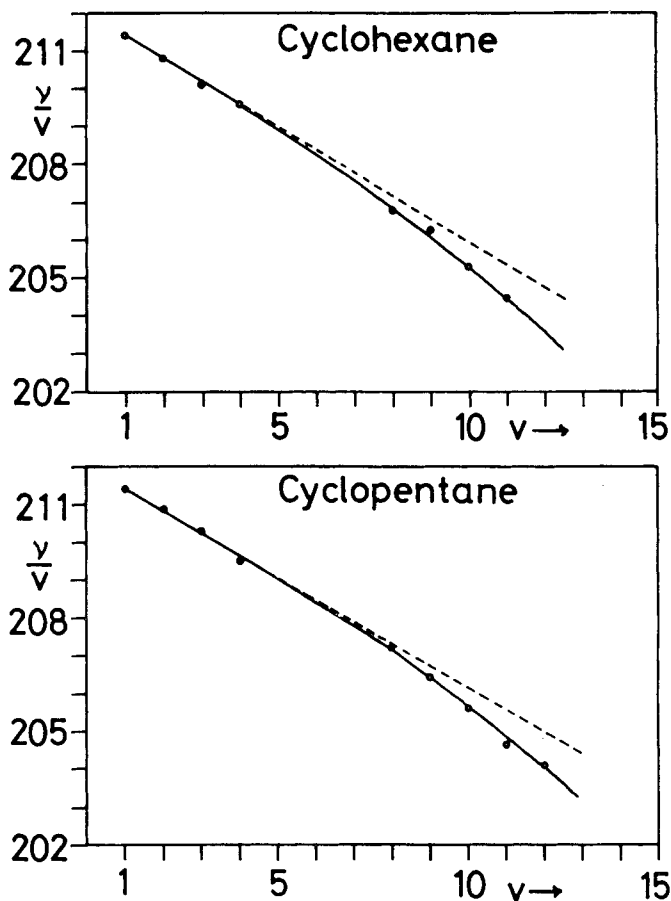


Fig. 8. Caption as in Figure 5 except for the solvents: cyclohexane and cyclopentane.

$\omega_e y_e$ , compared to the value for the gas phase [1] ( $\omega_e y_e = -0.0016 \text{ cm}^{-1}$ ) is observable.

Is it possible to say something about the intermolecular forces giving rise to the different spectroscopic constants as for example  $\text{I}_2$  in carbondisulfide compared with  $\text{I}_2$  gas? To answer this question one could look at the treatment given by Buckingham [14] for a diatomic oscillator in a field whose intermolecular potential is  $U$ . With a total potential energy for the diatomic molecule of the form

$$V = V_0 + U = \frac{k_0}{2} \Delta r^2 - g_0 \Delta r^3 + j_0 \Delta r^4 + U \quad (2)$$

one can write the change in  $\omega_e$  as

$$\frac{\Delta \omega_e}{\omega_e} = -\frac{3g_0}{k_0^2} U' - \frac{U''}{2k_0} \quad (3)$$

and the change\* in  $\omega_e x_e$  as

$$\frac{\Delta\omega_e x_e}{\omega_e x_e} = \frac{U'''}{3g_0} - 4 \frac{\Delta\omega_e}{\omega_e} \quad (4)$$

if  $\frac{2}{5}(j_0 k_0 / g_0^2)$  is small. The symbols are the same as those given in Reference 15. It is clear then that the sign and magnitude of  $\Delta\omega_e x_e$  depends on the third derivative of the intermolecular potential function. Unfortunately unless the form of  $U$  is known it is impossible to be quantitative. In the Appendix the derivatives of the intermolecular potential function are evaluated for Equation (2). While  $U'$  is realistic when evaluated from dispersion forces the value for  $U'''$  is not. This suggests inclusion of a repulsive interaction which is greater for  $U'''$  than for  $U'$ .

TABLE II  
Spectroscopic constants of the iodine stretching vibration in various solvents

Solvent	$\omega_e(\text{cm}^{-1})$	$\omega_e x_e(\text{cm}^{-1})$	$\omega_e y_e(\text{cm}^{-1})$	$\lambda_{\text{max}}(\text{\AA})$
Carbontetrachloride	$212.59 \pm 0.08$	$0.62 \pm 0.03$	$-0.005 \pm 0.002$	} ~ 5200
Cyclohexane	$212.57 \pm 0.10$	$0.60 \pm 0.04$	$-0.006 \pm 0.003$	
Cyclopentane	$212.55 \pm 0.10$	$0.58 \pm 0.04$	$-0.005 \pm 0.003$	
<i>n</i> -pentane	$212.56 \pm 0.10$	$0.56 \pm 0.04$	$-0.006 \pm 0.003$	
<i>n</i> -heptane	$212.51 \pm 0.10$	$0.56 \pm 0.04$	$-0.007 \pm 0.003$	
<i>n</i> -hexane	$212.24 \pm 0.10$	$0.53 \pm 0.04$	$-0.008 \pm 0.003$	
Chloroform	$212.18 \pm 0.08$	$0.64 \pm 0.03$	$-0.004 \pm 0.002$	
Chloroform <sup>a</sup>	$213 \pm 0.5$	$1 \pm 0.2$	—	
Carbonylsulfide	$207.80 \pm 0.12$	$0.48 \pm 0.03$	$-0.002 \pm 0.001$	
Benzene	$206.6 \pm 0.3$	$0.7 \pm 0.2$	—	
Toluene	$204.9 \pm 0.3$	$0.5 \pm 0.3$	—	
<i>p</i> -xylene	$204.8 \pm 0.3$	$0.8 \pm 0.3$	—	
<i>p</i> -dioxane	$204.8 \pm 0.3$	$0.5 \pm 0.3$	—	~ 4500
Gas <sup>b</sup>	$214.534 \pm 0.04$	$0.6070 \pm 0.0085$	$-0.0016 \pm 0.0008$	~ 5200

<sup>a</sup> Reference 6.

<sup>b</sup> Reference 1.

In the case of the strong interaction between iodine and the solvent (e.g. pyridine) only the fundamental and a weak overtone of the  $I_2$  vibration were found by excitation using the visible laser lines of the argon ion laser [9]. In this case, moreover, a RRE spectrum of the  $I_3^-$  ion can be detected [13], which is superimposed on an otherwise perhaps (when higher frequency laser lines are used [9]) observable RRS of the  $I_2$  vibration.

### 3.3. HALFBANDWIDTHS OF THE OVERTONE PROGRESSION

The halfbandwidths of the iodine fundamental and its overtone progression in various solvents are listed in Table III. We found that the increase in the widths at half height

\* Note that in the equation given in Reference 15 the term  $4\Delta\omega_e/\omega_e$  has been unjustifiably neglected.

TABLE III  
Half band widths of the overtones of iodine in various solvents (in  $\text{cm}^{-1}$ )

Solvent	Vibrational quantum number $\nu$													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1. Carbontetrachloride	2.4	4.5	8.3	-	21	37	39	46	63	73	83	83	99	91
2. Chloroform	2.1	4.9	9.2	13.8	28	-	39	58	66	66	75	-	-	-
Chloroform <sup>a</sup>	2.5	8	14	23	28	-	-	-	-	-	-	-	-	-
3. Carbondisulfide	2.2	6.3	-	-	39	-	54	60	72	72	81	81	92	102
4. <i>n</i> -pentane	2.0	4.7	8.1	-	-	30	-	38	44	50	62	-	-	-
5. <i>n</i> -hexane	2.3	4.7	8.5	-	-	26	-	38	43	52	58	-	-	-
6. <i>n</i> -heptane	2.0	5.1	10.1	16.3	-	-	-	42	48	56	64	-	-	-
7. Cyclopentane	2.1	4.8	11.9	14.6	-	-	-	39	46	55	66	-	-	-
8. Cyclohexane	2.0	5.1	8.8	12.2	-	-	-	46	45	50	-	-	-	-
Average 1.-3.	2.2	5.2	8.7	13.8	29	37	44	55	67	70	79	82	95	99
Average 4.-8.	2.1	5.9	9.5	14.4	-	28	-	41	45	53	62	-	-	-

<sup>a</sup> Reference 6.

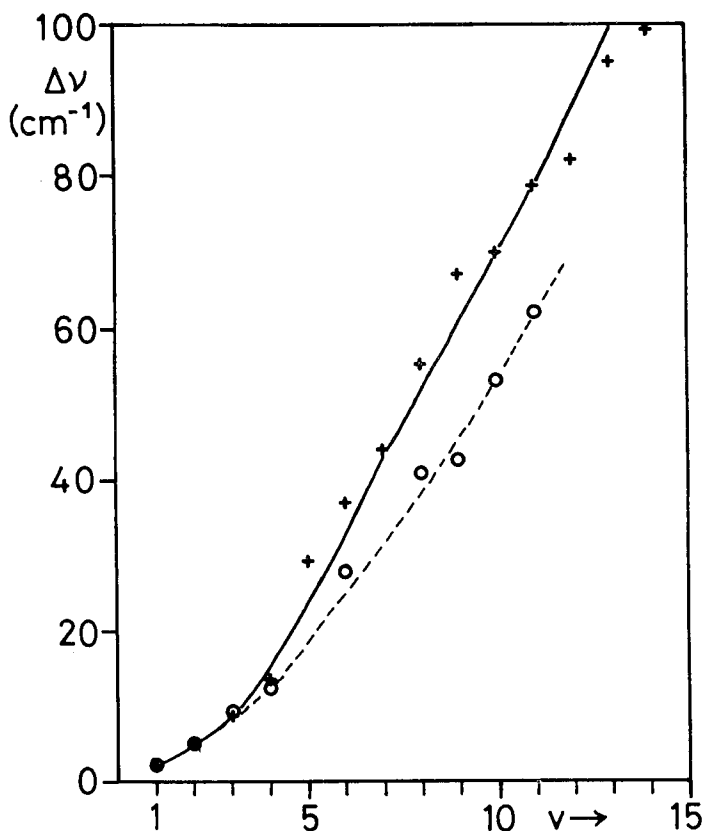


Fig. 9. The observed half-bandwidths of the iodine stretching vibration and its overtones in various solvents. The + signs are the average values corresponding to the solvents carbontetrachloride, chloroform and carbondisulfide. Circles correspond to the average values obtained in *n*-pentane, *n*-hexane, *n*-heptane cyclopentane and cyclohexane.

is similar for carbon tetrachloride, chloroform and carbondisulfide. We therefore took the average of corresponding vibrations and plotted these data in Figure 9 (crosses, solid line) vs the vibrational quantum number  $v$ . For the other solvents (*n*-pentane, *n*-hexane, *n*-heptane, cyclopentane and cyclohexane) also similar but in general slightly lower values than those for the smaller solvent molecules were found. The average data are also given in Table III and plotted in Figure 9 (circles, dotted line). It can be seen, that there is a nonlinear increase in half band width with higher  $v$ . The broadening of the Raman lines in the RRS of iodine gas has been satisfactorily explained in terms of the spreading of O-, Q- and S-branches and the observation of S-bandheads. In the liquid phase, however, the broadening can not be explained by this effect (as has been already mentioned above), because of the much lower spectroscopic temperature and the observation of a symmetric band profile. On the other hand, the symmetric band profile suggests that the observed broadening of the overtone progression may be due to relaxation processes. Collisions of the iodine molecule with solvent molecules may broaden the bands which correspond to  $I_2$  oscillations with double, triple, etc.,... frequencies. This is also indicated in the fact that the broadening is slightly different for simpler solvent molecules. Similar broadening of overtone progressions in the liquid and solid phase have been also observed in the  $MnO_4^-$  and  $CrO_4^{2-}$  ions [8].

#### 4. Conclusion

We have shown that the RRE provides a new and powerful method to derive spectroscopic constants of certain vibrations in the liquid phase with relatively high accuracy. In the case of the iodine molecule in various solvents no large changes in the constants  $\omega_e$  and  $\omega_e x_e$  were found for such solvents which do not form a charge transfer complex. In all cases a large increase in halfbandwidths with increasing vibrational quantum number was observed which possibly can be interpreted as collision broadening. More experimental work on these subjects, especially on molecules with other symmetries is in progress.

#### Acknowledgements

One of us (W.K.) wishes to acknowledge discussions with Prof. Brandmüller and Prof. Schrötter.

#### Appendix

The potential function used is

$$V = V_0 + U = \frac{k_0}{2} \Delta r^2 - g_0 \Delta r^3 + j_0 \Delta r^4 + U.$$

By differentiation with respect to the normal coordinate one obtains

$$\begin{aligned} U' &= -K_0 \Delta r \\ U'' &= -\Delta K + 6g_0 \Delta r \end{aligned}$$

$$U''' = 6\Delta g - 24j_0\Delta r$$

$$U'''' = -24\Delta j.$$

In these expressions

$$\Delta r = r_0^{\text{gas}} - r_0^{\text{soln}}$$

$$\Delta K = K_0^{\text{gas}} - K_0^{\text{soln}}$$

$$\Delta g = g_0^{\text{gas}} - g_0^{\text{soln}}$$

$$\Delta j = j_0^{\text{gas}} - j_0^{\text{soln}}.$$

The theory of the anharmonic oscillator gives

$$\omega_e x_e = \frac{3h}{32\pi^4 \omega_e^4 \mu^2 c^3} \left( \frac{5g^2}{8\pi^2 \omega_e^2 \mu C^2} - j \right)$$

$$\omega_e y_e = \frac{-17h^2 j^2}{1024\mu^4 \pi^8 C^6 \omega_e^5}.$$

From the data for  $I_2$  (Table II) in the gas phase and in  $CS_2$  solution one can evaluate the constants shown in Table IV.

TABLE IV

	Gas	$CS_2$ solution	$\Delta[\text{gas} - \text{soln}]$
$j_0$	$0.92 \times 10^{20}$	$0.88 \times 10^{20}$	$0.04 \times 10^{20}$
$g_0$	$9.65 \times 10^{12}$	$7.42 \times 10^{12}$	$2.23 \times 10^{12}$
$K_0$	$1.73 \times 10^5$	$1.62 \times 10^5$	$0.11 \times 10^5$
$\omega_e$	214.50	207.80	6.70
$\omega_e x_e$	0.607	0.48	0.127
$\omega_e y_e$	-0.0016	-0.0020	0.0004

From the (gas-solution) differences one evaluates

$$U'''' = -0.96 \times 10^{20}$$

$$U''' = 13.4 \times 10^{12} - 22.1 \times 10^{20} \Delta r$$

$$U'' = -0.125 \times 10^5 + 58.0 \times 10^{12} \Delta r$$

$$U' = -1.73 \times 10^5 \Delta r$$

For an intermolecular potential which is essentially for attraction between molecules

$$U = -B \cdot \alpha_1 \quad \text{with} \quad B = \frac{3}{2} \frac{\alpha_2 I_2 I_1}{R^6 (I_1 + I_2)},$$

where

$\alpha_1$  = polarizability of solute

$\alpha_2$  = polarizability of solvent

$I_1$  = ionization potential of the solute

$I_2$  = ionization potential of the solvent

$R$  = the distance between molecular centers of solute and solvent.

If  $I_1/(I_1 + I_2)$  is nearly constant for a variety of solvents, then differentiation gives

$$U' = -B\alpha_1^1.$$

Hence

$$\frac{U'}{U} \approx \frac{\alpha^1}{\alpha}.$$

The interaction energy between nonpolar molecules is of the order of 1 kcal mole<sup>-1</sup>. For  $I_2$ ,  $\alpha = 3.5 \times 10^{-24}$  and  $\alpha^1$  is about  $1.7 \times 10^{-16}$ , hence

$$U' = 7 \times 10^{-14} \times \frac{1}{2} \times 10^9 = 3.5 \times 10^{-6} \text{ cgs.}$$

Equating this to  $-1.73 \times 10^5 \Delta r$  gives

$$\Delta r = -0.002 \text{ \AA} \quad \text{or} \quad -2 \times 10^{-11} \text{ cm.}$$

Using this value of  $\Delta r$  we find

$$U'' = -0.137 \times 10^5$$

$$U''' = 13.8 \times 10^{12}$$

$$U'''' = -0.96 \times 10^{20}$$

all in cgs units

Since the sign of  $U'''$  would be  $-v^e$  for dispersion forces only, perhaps a repulsion term is required to give the  $+v^e$  sign observed for  $U'''$ .

The same conclusion is obtained if the term in  $j_0 \Delta r^4$  is neglected. The only change is for  $U'''$  which becomes 3% smaller.

### References

1. Kiefer, W. and Bernstein, H. J.: *J. Mol. Spectry.* **43**, 366 (1972).
2. Kiefer, W. and Bernstein, H. J.: *J. Chem. Phys.* **57**, 3017 (1972).
3. Rank, D. H. and Rao, B. S.: *J. Mol. Spectry.* **13**, 34 (1964).
4. Holzer, W., Murphy, W. F., and Bernstein, H. J.: *J. Chem. Phys.* **52**, 399 (1970).
5. Beattie, I. R., Ozin, G. A., and Perry, R. O.: *J. Chem. Soc. A*, 2071 (1970).
6. Mortensen, O. S.: *J. Mol. Spectry.* **39**, 48 (1971).
7. Kiefer, W. and Bernstein, H. J.: *Appl. Spectrosc.* **25**, 500 (1971).
8. Kiefer, W. and Bernstein, H. J.: *Mol. Phys.* **23**, 835 (1972).
9. Kiefer, W. and Bernstein, H. J.: to be published.
10. Kiefer, W.: *Appl. Spectrosc.* **27**, 253 (1973).
11. Herzberg, G.: *Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules*, D. van Nostrand Company, Inc. (1964).
12. Rosen, H., Shen, Y. R., and Stenman, F.: *Mol. Phys.* **22**, 33 (1971).
13. Kiefer, W. and Bernstein, H. J.: *Chem. Phys. Letters* **16**, 5 (1972).
14. Buckingham, A. D.: *Trans. Farad. Soc.* **56**, 753 (1960).
15. Perrot, M., Turrell, G., and Van Huong, P.: *J. Mol. Spectry.* **34**, 47 (1970).