

H. STAMMREICH AND THE TRIPLE ALLIANCE: THE MOLECULE, THE PROBLEM AND THE INSTRUMENT

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Almost 60 years ago H. Stammreich obtained the Raman spectra of two photosensitive molecules, Cl_4 and SnI_4 , using a pioneering technology developed by him. At the time the excitation source was homemade gas lamps. The same experiments were repeated by us, with the best technology available, with outstanding correlation, and some new information was obtained that wasn't possible 60 years ago. The major difference between the experiments was the use of laser, that made the Raman spectroscopist's life much easier and less time-consuming.

Keywords: H. Stammreich; Raman spectra; tin tetraiodide; carbon tetraiodide.

INTRODUCTION

Carbon tetraiodide and tin tetraiodide, whose Raman spectra were investigated by H. Stammreich almost 60 years ago, are highly symmetrical molecules with chemical bonds strongly polarizable what implies very high Raman intensities. Besides both molecules, but mostly the former, are light-sensitive what precludes obtaining the Raman spectra at wavelengths shorter than ca. 600 nm. Given that Stammreich laboratory was a pioneer and one of the few to use long-wavelength excitation, such molecules were ideal for a Raman study using his instrumentation. It should also be considered that in both molecules there are normal modes that appear at very low frequencies, of the order of 100 cm^{-1} or lower and their detection demands a Raman instrument capable to reach a region very close to the Rayleigh wing.

Group IV tetrahalides were the object of several studies and, in particular, two previous publications deserve special attention since they were published before and after Stammreich paper. Woodward and Long¹ investigated the Raman intensities of MCl_4 ($\text{M} = \text{C}, \text{Si}, \text{Ge}$ and Sn) and XBr_4 ($\text{X} = \text{C}$ and Sn), using as excitation Hg lamp and photographic detection. Cl_4 and SnI_4 were excluded due to their photosensitivity. The main focus of this work was the verification of the relation between bond polarizability and Raman intensity, as predicted by Placzek theory.² It is expected that Placzek theory is a very good approximation for the calculation of Raman intensities, provided that the vibrational mode in question is the symmetrical stretching of spherically symmetrical molecules, such as the group IV tetrahalides, and provided that excitation is far from resonance. On the other hand a resonance Raman study on the carbon, silicon, germanium and tin tetraiodides was performed by Clark and Dines,³ using several laser excitation lines in the visible and ultraviolet. In this paper the authors comment on Stammreich's publication on carbon tetraiodide, and highlighted the photo instability of Cl_4 in wavelengths shorter than c.a. 570 nm. The agreement of Stammreich Raman shifts for Cl_4 and those reported by Clark and Dines is perfect within 1 cm^{-1} . The assignment proposed is also the same as previously done by Stammreich *et al.*, which is remarkable taking into account the homemade equipment with photographic detection and He lamp excitation as compared with spectra obtained in a double monochromator, laser excitation and photomultiplier detection. It should be pointed out that the main focus of Clark and Dines was to

investigate the resonance Raman effect in group IV tetrahalides using several visible and UV laser lines. In the case of SnI_4 , excitation at resonance resulted in the observation of several overtones of the ν_1 mode up to $9\nu_1$. For Cl_4 such investigation was not possible due to the extreme photosensitivity in lower wavelengths.

Concerning relative intensities and bandwidths the comparisons are much more difficult since the photographic plate is not linear with respect to recording intensities, and linewidths depend strongly on resolution and, in the case of solutions, on the solvents used. Such parameters can be accurately determined in present days, but were out of the reach of the older instrumentation.

Concerning the comparison of the spectral resolution reported in Stammreich papers, 0.8 cm^{-1} , with those in Clark and Dines where the spectral resolution is reported as c.a. 5 cm^{-1} . These figures can seem odd at first sight. In fact, 0.8 cm^{-1} was the limit resolution attainable, but the width of the Raman lines for samples in condensed phase is much higher, implying that the effective resolution was of the order c.a. $5 - 7\text{ cm}^{-1}$.

Concerning Raman bands below 100 cm^{-1} , recorded by Stammreich for Cl_4 (90 cm^{-1}) and SnI_4 (47 and 62 cm^{-1}), assigned to bending modes that show up at such low-frequency region given the presence of heavy atoms and low force constants. Reaching such low-frequency region using a spectrograph is another indication of the excellent optical design of Stammreich instrumentation. With present-day instrumentation, at the state of the art, it is possible to reach even lower frequencies, as it'll be shown in what follows. The assignment of such bands is not so straightforward since, in the case of solids, such region is the one where lattice modes are expected. Such modes are expected to disappear in the spectrum of the solution.

Taking into account that over the last 60 years enormous progress in Raman instrumentation has occurred, a question applies: is the quality of the Raman spectra of such molecules obtained with state of the art instrumentation qualitatively different from the ones obtained by Stammreich and coworkers? The present work aims to answer such question.

EXPERIMENTAL SECTION

Carbon tetraiodide was purchased from Sigma-Aldrich and used as received. Tin tetraiodide was synthesized combining elemental iodine and elemental tin, in a molar ratio of 2:1, in hexane. The solution was kept under reflux until an orange solid appeared. For further purification, the solid was recrystallized in hexane.

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The Raman spectra were obtained with the samples in the solid state in a Horiba-Jobin-Yvon T64000 triple monochromator spectrometer equipped with a CCD, using a backscattering geometry. Excitation source was provided by an diode laser Cobalt Flamenco™ 200 of 660 nm with a typical output power of 380 mW. The spectrometer is coupled to a microscope, what greatly increases the power density at the sample; the power was ca. 10 mW. An optical slit of 100 μm was used to give a spectral resolution of approximately 0.8 cm^{-1} . The exposure time for Cl_4 was 10 s, and for SnI_4 was 5 s.

It is important to mention that photodecomposition was not observed since there was no modification of the image observed in the microscope. In this experimental setup it was possible to observe the Raman spectra down to 10 cm^{-1} .

In the spectra reported by Stammreich *et al.* frequencies down to ca. 50 cm^{-1} are reported as compared to ca. 10 cm^{-1} we observed. It must be emphasized that the instrument used in the present paper is a triple monochromator in the subtractive mode, where the first stage is a filter permitting to reach wavenumbers very close to the Rayleigh wing. In Stammreich instrumentation a spectrograph was used with just one stage.

RESULTS AND DISCUSSION

The Raman spectrum of Cl_4 , obtained in the present work, is shown in figure 1. The Raman wavenumbers are listed in table 1 together with the obtained by Stammreich *et al.*⁴ As can be seen the agreement is remarkable. It should be mentioned that in the investigation of Clark and Dines³ involving the Raman spectra of tetraiodides of group IV elements the agreement is also remarkable with Stammreich results, including the assignment of the observed bands.

The Raman spectrum of SnI_4 is shown in Figure 2. The Raman wavenumbers are listed in table 2 together with the obtained by

Table 1. Table of frequencies of Cl_4

Stammreich <i>et al.</i> (1961) Exposure time: ca. 4 h	Our results Exposure time: 10 s	Assignment
90 cm^{-1}	89 cm^{-1}	ν_2 (e)
123 cm^{-1}	123 cm^{-1}	ν_4 (f_2)
178 cm^{-1}	179 cm^{-1}	ν_1 (a_1)

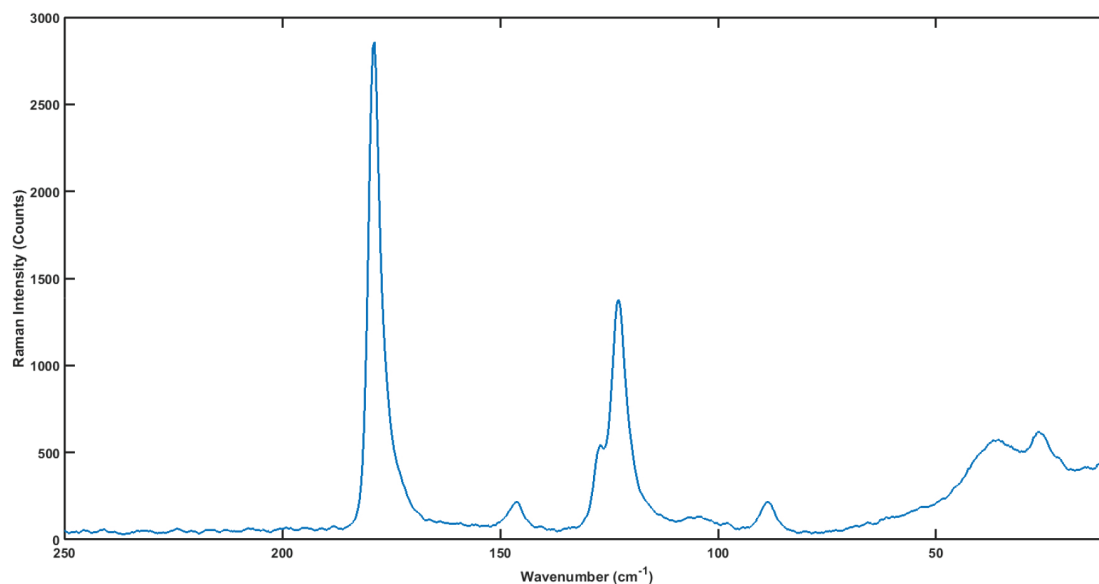


Figure 1. Raman spectrum of carbon tetraiodide within the region of 10 to 250 cm^{-1}

Stammreich *et al.*⁵ As can be seen the agreement is remarkable. Again, it should be mentioned that in the investigation of Clark and Dines³ involving the Raman spectra of tetraiodides of group IV elements the agreement is also remarkable with Stammreich results, including the assignment of the observed bands.

Table 2. Table of frequencies of SnI_4

Stammreich <i>et al.</i> (1956) Exposure time: ca. 10 min	Our results Exposure time: 5 s	Assignment
47 cm^{-1}	52 cm^{-1}	ν_2 (e)
62 cm^{-1}	64 cm^{-1}	ν_4 (f_2)
149 cm^{-1}	147 cm^{-1}	ν_1 (a_1)
216 cm^{-1}	216 cm^{-1}	ν_3 (f_2)

Another point to be compared concerns the exposure time for the obtention of the spectra: in the case of SnI_4 was about 30 minutes in Stammreich spectrum and about 5 seconds in our case. It should be pointed out that in the former case the spectrum obtained was of a concentrated solution in CS_2 and our spectrum was of the sample in the solid-state. In the case of Cl_4 , Stammreich spectrum was recorded with up to 15 hours of exposure, due to the extreme photosensitivity of the sample, what required a continuous renovation of the sample.

One of the difficulties in obtaining the Raman spectra of Cl_4 and SnI_4 is the presence of bands at rather low wavenumbers, as for instance a band at ca. 47 cm^{-1} in the spectrum of SnI_4 , since the Rayleigh wing would preclude the accurate measurement. In this respect Stammreich *et al.* were able to record a Raman band at ca. 47 cm^{-1} , that is the lowest wavenumber assignable to a normal mode of SnI_4 . With our equipment, in the triple monochromator configuration, it was possible to reach about 10 cm^{-1} . The comparison with the spectrum obtained by Stammreich *et al.* shows how close to the Rayleigh wing they could get, what is remarkable since the equipment used was a single stage spectrograph.

The instrumentation developed by Stammreich and coworkers was to a great extent homemade. It is important to know several details that normally are not reported in their papers. Fortunately most of such details were reported in a publication that is an example of the state of the art of experimental spectroscopy at those days.⁶ It is

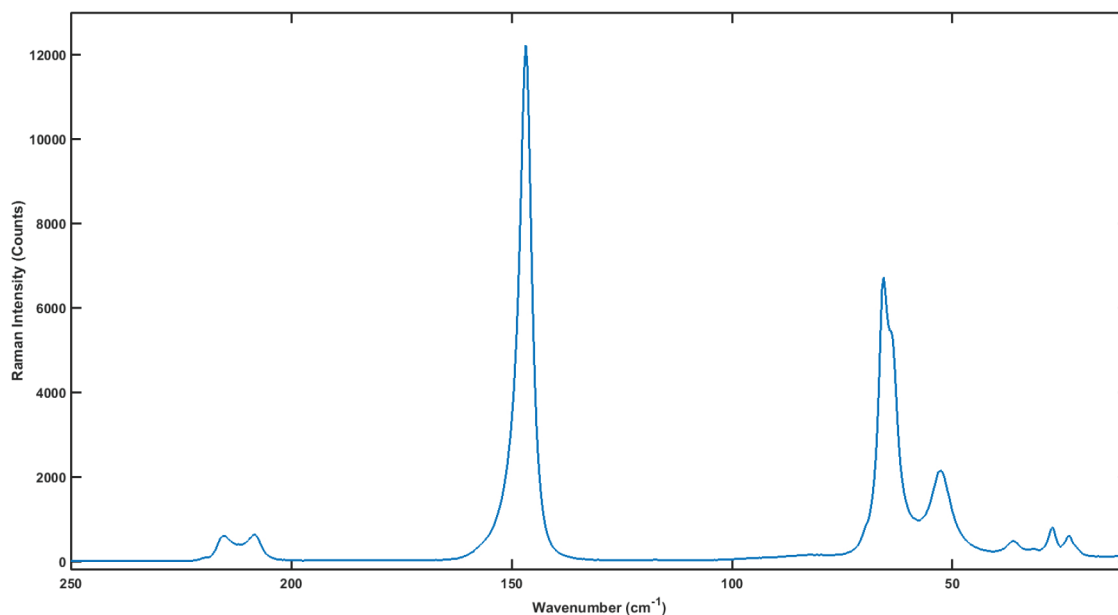


Figure 2. Raman spectrum of tin tetraiodide within the region of 10 to 250 cm^{-1}

highly recommended for those interested in the evolution of Raman spectroscopy instrumentation over the years.

CONCLUSIONS

Taking into account that the spectra were obtained more than 60 years ago by H. Stammreich *et al.*, the agreement is outstanding. The use of lasers and other technologies changed the entire scenario of Raman spectroscopy, but one should not forget that the pioneering methods developed by H. Stammreich were very important by that time. Despite the enormous advances in instrumentation over the years, the reading of Stammreich papers shows a very careful analysis of the results, what is becoming increasingly rare at present days.

AGRADECIMENTOS

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