# Resonance Raman Spectrum of Tin Tetraiodide

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*Summary* By use of 363·8 nm excitation of an argon ion laser, and appropriate optics, cyclohexane solutions of tin tetraiodide exhibit a high intensity overtone progression in $\nu_1$ ($a_1$) out as far as $11\nu_1$.

THE Raman spectra of molecular species are normally obtained under conditions in which $\nu_0$, the exciting frequency, is well removed from $\nu_e$, the frequency of the first allowed electronic transition in the molecule. As $\nu_0$ is allowed to approach $\nu_e$, one first observes the pre-resonance Raman effect (pre-RRE) when $\nu_0$ is close to, but not actually within the absorption band; the characteristic features of pre-RRE are the enhanced intensities of certain fundamentals. The RRE may be observed when $\nu_0$ is within the contour of the absorption band, and this effect is characterised by high intensity overtone progressions of usually a single fundamental.[1]

The Raman spectrum of tin tetraiodide, a deep orange molecular species, is well known, the fundamental frequencies being[2] $\nu_1$ ($a_1$) 151, $\nu_2$ ($e$) 43, $\nu_3$ ($t_2$) 221, $\nu_4$ ($t_2$) 63 cm$^{-1}$; these data were obtained by use of 647·1, 568·2, or 514·5 nm excitation. The pre-RRE is displayed with the 568·2 and 514·5 nm exciting lines.[2] Higher frequency exciting lines resulted in decomposition of the molecule. We have now discovered that by use of the rotating sample technique,[3,4] whereby the sample is rotated at speeds of *ca.* 1600 r.p.m., no sample decomposition takes place even with higher frequency exciting lines. Indeed, we have succeeded in obtaining a resonance Raman spectrum of tin tetraiodide (0·06M in cyclohexane) using 363·8 nm excitation (Ar$^+$, *ca.*

TABLE

The $\nu_1$ ($a_1$) fundamental frequency, and its overtones, of tin tetraiodide in cyclohexane (cm$^{-1}$)

| Band | Frequency | $n\nu_1/n$ | $\Delta\nu$[a] |
|---|---|---|---|
| $\nu_1$ | 151 | 151 | 24 |
| $2\nu_1$ | 302 | 151 | 27 |
| $3\nu_1$ | 453 | 151 | 29 |
| $4\nu_1$ | 602 | 150·5 | 31 |
| $5\nu_1$ | [759·5][b] | [151·9] | — |
| $6\nu_1$ | 903·5 | 150·6 | 37 |
| $7\nu_1$ | 1053·5 | 150·5 | [50] |
| $8\nu_1$ | 1204·5 | 150·6 | 51 |
| $9\nu_1$ | 1355·5 | 150·7 | 60 |
| $10\nu_1$ | 1506 | 150·6 | — |
| $11\nu_1$ | 1653 | 150·3 | — |

[a] Half band width. [b] The value of $5\nu_1$ can only be estimated owing to near coincidence with the (slightly weaker) 806 cm$^{-1}$ band of cyclohexane.

20 mW) *i.e.* using an exciting frequency (27,487 cm$^{-1}$) which virtually coincides with the maximum of the first allowed electronic transition of the molecule (27,435 cm$^{-1}$).[2]

Despite the fact that the spectrometer (Spex 1401) is optimized for work at 500 nm, we obtained a resonance Raman spectrum of tin tetraiodide, the overtone progression of $\nu_1$ ($a_1$) extending out to $11\nu_1$ and overlying a fluorescent background centred at *ca.* 450 cm$^{-1}$. The results are given in the Table, from which it is apparent that this fundamental mode is almost exactly harmonic. This situation parallels that recently reported for titanium tetraiodide, for which an overtone progression in $\nu_1$ ($a_1$) out to $12\nu_1$, was observed by use of 514·5 nm excitation ($\nu_0 = 19{,}435$ cm$^{-1}$, $\nu_e = 19{,}400$ cm$^{-1}$) and for which $\omega_1 = 161{\cdot}2$ cm$^{-1}$ and $X_{11} = 0{\cdot}11$ cm$^{-1}$. Calibration difficulties in the range in question precluded our obtaining comparably accurate values for $\omega_1$ and $X_{11}$ of tin tetraiodide; however, the values are estimated to be $150{\cdot}1 \pm 0{\cdot}5$ and $0{\cdot}05 \pm 0{\cdot}05$ cm$^{-1}$, respectively. The relative intensities of the overtones are $\nu_1 \sim 2\nu_1 \sim 3\nu_1 \sim 4\nu_1 \sim 5\nu_1 > 6\nu_1 \sim 7\nu_1 > 8\nu_1 > 9\nu_1 > 10\nu_1 \sim 11\nu_1$; this unexpected intensity progression occurs owing to the fact that the higher overtones lie in increasingly more favourable regions of the spectral response curve of the instrument. Thus the overtones display the following features characteristic of the RRE as distinct from resonance fluorescence: (a) continuous decrease in relative intensities (corrected for spectral response) with increase in vibrational quantum number ($n$), and (b) continuous increase in half-band width with increase in $n$ (*cf.* Table). In agreement with the theory of Nafie *et al.*,[6] it is only the totally symmetric vibration which shows the RRE.

It is evident that, by extended and more detailed studies of the RRE in simple molecules, it should be possible to obtain good information on the degree of anharmonicity of totally-symmetric fundamentals.

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