Resonance Raman and Preresonance Raman Spectra of Titanium Tetraiodide

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Abstract: The Raman spectrum of titanium tetraiodide has been recorded using nine excitation frequencies and the rotating sample technique. The spectrum is normal with 647.1 nm excitation, the relative intensities of the fundamentals being $\nu_1(a_1) \gg \nu_3(t_2) \sim \nu_2(e) > \nu_4(t_2)$. However, as the excitation frequency approaches that of the first allowed electronic transition, both $\nu_1(a_1)$ and $\nu_3(t_2)$ exhibit preresonance enhancement to their intensities. For 514.5 and 488.0 nm excitation, a resonance Raman spectrum of the molecule is obtained, high intensity overtone progressions out to $13\nu_1$ being observed. Harmonic frequencies and anharmonicity constants for the $\nu_1(a_1)$ fundamental have been determined and titanium–iodine bond polarizability derivatives are reported.

When the exciting frequency is well removed from the resonance region and both the initial and final states of the molecule are in the ground electronic state, Placzek[1] has shown that the intensity of molecular Raman scattering arises from the dependence of the ground-state polarizability on nuclear vibrations. As the exciting frequency is made to approach the first allowed electronic transition in the molecule, Albrecht[2–5] has predicted that those normal modes which are vibrationally active in the electronic transition (*i.e.*, most responsible for "forbidden" intensity in the allowed transitions) should exhibit a striking enhancement of their Raman intensities. Recently, Innes, *et al.*,[6] have confirmed this prediction in the case of the 320-nm $^1B_{3u}$–^1A_g system of pyrazine; the $\nu_5(b_{2g})$ vibration of this molecule is known to mix the intensity of a stronger $^1B_{1u}$–^1A_g transition with the 320-nm transition, and the same vibration was shown to display the preresonance Raman effect (pre-RRE). Unfortunately, such a complete study is not possible in the case of the molecular tetrahalides, because no vibrational structure has been observed let alone analyzed in respect to their first allowed electronic transitions.

In previous Raman spectroscopic investigations of the molecular tetrahalides MX_4 (M = C, Si, Ge, or Sn; X = Cl, Br, or I), $TiCl_4$, $TiBr_4$,[7,8] and VCl_4,[9] it has been shown that the Raman bands assigned to the $\nu_1(a_1)$ and $\nu_3(t_2)$ fundamentals, but not those assigned to the $\nu_2(e)$ and $\nu_4(t_2)$ fundamentals, increase in intensity as the exciting frequency (ν_0) is made to approach that of the first allowed electronic transition (ν_e) of the molecule. By contrast to the pre-RRE, if the exciting frequency falls within the contour of the absorption band associated with an allowed electronic transition of the molecule, a resonance Raman effect (RRE) should be observed. The RRE is characterized by an apparent breakdown in the harmonic oscillator selection rules whereby vibrational overtones may appear with intensities comparable with that of the fundamental.[10]

It has been clear for several years that titanium tetraiodide, with its first allowed electronic transition at 19,400 cm^{-1},[11] would be likely to exhibit the RRE with many exciting lines of the Ar$^+$ and Kr$^+$ lasers, and most especially with 514.5 nm (19,435 cm^{-1}) excitation for which $\nu_0 - \nu_e$ is only 35 cm^{-1}. An earlier attempt to observe the RRE with titanium tetraiodide failed owing to decomposition of the compound at the beam focus.[12] It is now apparent that this decomposition was thermal rather than photochemical, because by use of the rotating sample technique[13,14] whereby the sample is rotated at *ca.* 1600 rpm, no decomposition takes place even when using the maximum power available at 514.5 nm ($\leq$1.9 W). Instead, a resonance Raman spectrum of titanium tetraiodide has been observed, both for the molecule in the solid state as well as in three different solvents, and long progressions of overtones of the $\nu_1(a_1)$ fundamental are observed. This has allowed a determination of the anharmonicity of this fundamental with considerable accuracy. The relationship between overtone intensities and the extinction coefficient of the molecule at ν_0 is delineated, and bond polarizability derivatives are calculated.

Experimental Section

Preparation of Samples. Titanium tetraiodide was purified by four consecutive sublimations in order to ensure that the halide was completely free of iodine.

Cyclohexane and carbon tetrachloride were kept over calcium hydride and then distilled directly into the sample cell. Carbon disulfide was likewise distilled directly into the sample cell. The solutions were made up by vacuum-line techniques and sealed into cylindrical Pyrex cells (volume *ca.* 12 ml) which had flat bottoms and which could be rotated at *ca.* 1600 rpm. This procedure eliminated thermal decomposition of the sample at the beam focus. The exciting beam was kept as close as possible to the cell edge in order to minimize self-absorption of the scattered radiation.

The solid-state spectra were obtained by subliming the halide onto the flat surface of a cell similar to that described above,

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(1) G. Placzek and E. Teller, *Z. Phys.*, **81**, 209 (1933).

(2) A. C. Albrecht, *J. Chem. Phys.*, **34**, 1476 (1961).

(3) J. Behringer in "Raman Spectroscopy," Vol. 1, H. A. Szymanski, Ed., Plenum Press, New York, N. Y., 1967, p 168.

(4) J. Tang and A. C. Albrecht in "Raman Spectroscopy," Vol. 2, H. A. Szymanski, Ed., Plenum Press, New York, N. Y., 1970, p 33.

(5) A. C. Albrecht and M. C. Hutley, *J. Chem. Phys.*, **55**, 4438 (1971).

(6) A. H. Kalantar, E. S. Franzosa, and K. K. Innes, *Chem. Phys. Lett.*, **17**, 335 (1972).

(7) R. J. H. Clark and C. J. Willis, *Inorg. Chem.*, **10**, 1118 (1971).

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(9) R. J. H. Clark, B. K. Hunter, and P. D. Mitchell, *J. Chem. Soc., Faraday Trans. II*, 476 (1972).

(10) W. Holzer, W. F. Murphy, and H. J. Bernstein, *J. Chem. Phys.*, **52**, 399 (1970).

(11) R. J. H. Clark and C. J. Willis, *J. Chem. Soc. A*, 838 (1971).

(12) R. J. H. Clark and B. K. Hunter, unpublished work, 1970.

(13) W. Kiefer and H. J. Bernstein, *Appl. Spectrosc.*, **25**, 501 (1971).

(14) R. J. H. Clark, *Spex Speaker*, **18**, 1 (1973).

sealing the cell, and then likewise rotating it at *ca.* 1600 rpm in order to obtain a Raman spectrum without sample decomposition.

Instrumentation. The Raman spectra were recorded by use of a Spex 1401 spectrometer with Coherent Radiation Model 52 Ar^+ and Kr^+ lasers. The scattered radiation was collected at 90° and focused by a f/0.95 lens onto the entrance slit of the monochromator after having been passed through a polarization scrambler. The 0.75 m Czerny-Turner monochromator employed two 1200 lines/mm Bausch and Lomb gratings blazed at 500 nm. The method of detection was photon counting in conjunction with an RCA C31034 phototube (linear display). The power available (prior to the insertion of the interference filter) at 457.9, 482.5, 488.0, 514.5, 520.8, 568.2, and 647.1 nm was 30 mW, 50 mW, 1.6 W, 1.9 W, 100 mW, 250 mW, and 500 mW, respectively. The spectra were calibrated by reference to the emission lines of neon and argon.

Two of the exciting wavelengths, 598.3 and 622.4 nm, were obtained by use of a Coherent Radiation Model 490 tunable dye laser in conjunction with the Model 52 Ar^+ laser as pump. The dyes employed were Rhodamine 6G and Rhodamine B, respectively, and the power available was *ca.* 400 and *ca.* 250 mW, respectively.

Peak areas were determined in most cases by the cutting and weighing procedure, the noise (particularly for the higher overtones) being too high in general to allow the use of electronic techniques.

The relative spectral response of the instrument was obtained by use of a tungsten strip lamp, the relative spectral radiance of which was determined at a brightness temperature of 2073° by comparison with a standard lamp.[15] This comparison was carried out at the National Physical Laboratory, Teddington.

Results and Discussion

Normal Raman Spectrum. The nature of the Raman spectrum of titanium tetraiodide is found to depend markedly on the exciting frequency, and in particular on the energy gap ($\nu_0 - \nu_e$) between the exciting frequency and the first allowed electronic transition of the molecule. The relationship between the exciting frequencies used, and the electronic spectrum of the molecule, is indicated in Figure 1.

The Raman spectrum of titanium tetraiodide in solution has been obtained previously by use of 647.1 nm excitation of a Kr^+ laser[11] and by use of 694.3 nm excitation of a quasicontinuous ruby laser.[16] The results were in excellent agreement with one another and also with the present work. The relative intensities of the fundamentals are $\nu_1 \gg \nu_3 \sim \nu_2 > \nu_4$. In addition, however, we have been able to obtain the solid-state Raman spectrum of the molecule. The results are given in Table I, in which they are compared with previously obtained infrared results.[11] Titanium tetraiodide is reported,[17] on the basis of powder diffraction data, to be dimorphic and to undergo a phase change at 100–125°; the room temperature form is reported to be of lower symmetry than the high temperature form, which is cubic with a cell dimension 12.21 Å. These results appear to be at variance with earlier results which were interpreted on the basis that titanium tetraiodide crystallizes in the cubic space group T_h^6 (*Pa* 3) with cell dimension 12.00 Å and eight molecules per unit cell. The site symmetry of the titanium atom is thus C_3. The present Raman results are consistent with this space group if the intermolecular forces are such that site group splitting but not correlation splitting of fundamentals is observable; *i.e.*, the $\nu_1(a_1)$ and $\nu_2(e)$ fundamentals are not split, but the $\nu_3(t_2)$ fundamental appears as a doublet in both the Raman and the infrared spectra (Table II). Clearly, however, low-temperature spectroscopic results as well as single-crystal X-ray diffraction data are required for a definitive structural statement on this molecule.

Table I. Fundamental Frequencies of Titanium Tetraiodide (647.1 nm excitation)

State	Technique	$\nu_1(a_1)$	$\nu_2(e)$	$\nu_3(t_2)$	$\nu_4(t_2)$
C_6H_{12} soln	Raman	161.3 (p) vs[a]	51 w	322 vw	n.o.[b]
	Ir	Inactive	Inactive		n.o.
Solid	Raman	160.8 vs	56 wm	319 w 309.5 vw	67.5 w
	Ir	Inactive	Inactive	320 vs 312 vs	67 wm

[a] This frequency was also checked carefully using 514.5 nm excitation. [b] n.o. = not obtained owing to the low intensity of this fundamental and to inadequate solubility of the molecule in cyclohexane.

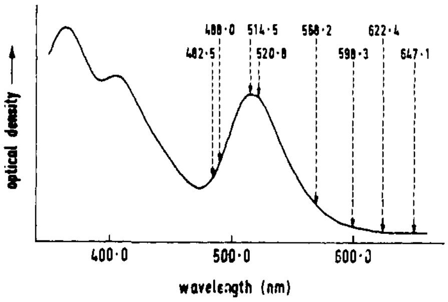

Figure 1. Electronic spectrum of titanium tetraiodide in relation to the exciting wavelengths used in the present study.

Table II. Factor Group Analysis on Titanium Tetraiodide on the Basis of the Space Group T_h^6 (*Pa* 3), $Z = 8$

Molecular symmetry T_d[a]	Site symmetry C_3[b]	Factor group T_h[c]
a_1	a_1	$a_g + t_g + a_u + t_u$
e	e	$e_g + e_u + 2t_g + 2t_u$
t_2	a + e	$a_g + a_u + e_g + e_u + 3t_g + 3t_u$

[a] In T_d, a_1, e, and t_2 are Raman active, t_2 is infrared active. [b] In C_3, a_1 and e are both Raman and infrared active. [c] In T_h, a_g, e_g, and t_g are Raman active, t_u is infrared active.

Preresonance and Resonance Raman Spectra. As the exciting wavelength is changed from 647.1 to 622.4, 598.3, 568.2, 520.8, and then to 514.5 nm, the intensities of the $\nu_1(a_1)$ and the $\nu_3(t_2)$ bands are appreciably enhanced relative to the 806 cm^{-1} peak (Figure 2) of cyclohexane. In the case of the $\nu_3(t_2)$ band (which coincides with $2\nu_1$, for which $\rho = 0$), the intensity increase was determined by measuring the intensity of its perpendicular component ($\rho = 0.75$) relative to the reference peak; a 20-fold enhancement occurs on changing from 647.1 to 514.5 nm excitation.

In addition to the enhancement of the $\nu_1(a_1)$ band, as ($\nu_0 - \nu_e$) is decreased, overtones of ν_1 begin to appear. For 514.5 nm excitation, for which $\nu_0 - \nu_e$ is only 35 cm^{-1}, high intensity overtone progressions occur both for the molecule in the solid state as well as in solution. For the solid state, the progression is observed to reach $12\nu_1$ (Figure 3), whereas for cyclohexane, carbon di-

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(15) T. J. Quinn and C. R. Barber, *Int. J. Sci. Metrology*, **3**, 19 (1967).

(16) W. Kiefer and H. W. Schrötter, *Z. Naturforsch.*, **25**, 1374 (1970).

(17) R. F. Rolsten and H. H. Sisler, *J. Amer. Chem. Soc.*, **79**, 5891 (1957).

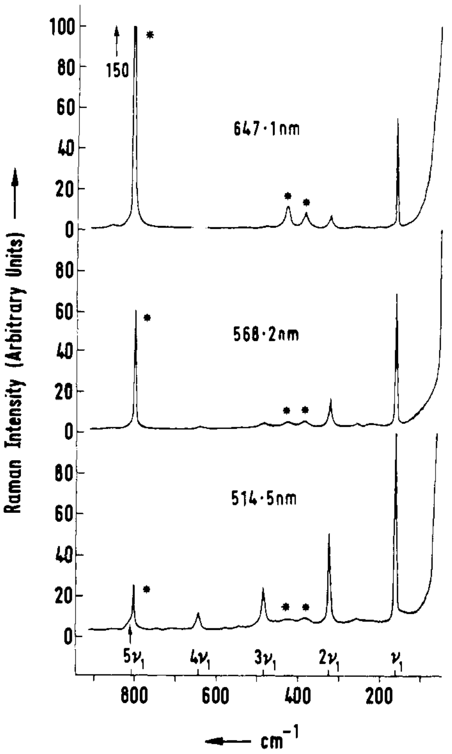

Figure 2. Raman spectra of titanium tetraiodide in cyclohexane obtained with 647.1, 568.2, and 514.5 nm excitation (laser powers adjusted so as to bring all spectra to the same scale). Slit widths 150/200/150 μ (2-3 cm^{-1}), gain 20K (1K = 1000 counts/sec), time constant (tc) 1 sec, scanning speed 10 cm^{-1}/min. Solvent peaks are marked with an asterisk, and overtones as $n\nu_1$.

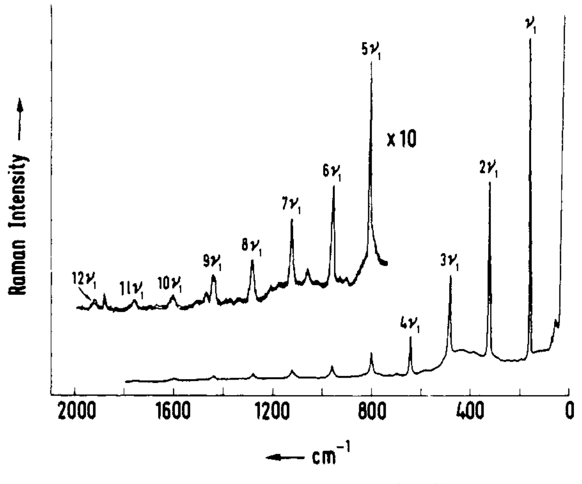

Figure 3. Resonance Raman spectrum of solid titanium tetraiodide obtained by use of 514.5 nm excitation. Slit widths 170/300/170 μ, gain 10K (inset 1K), tc 1 sec, scanning speed 25 cm^{-1}/min.

sulfide,[18] and carbon tetrachloride solutions it is observed to reach $10\nu_1$, $9\nu_1$, and $6\nu_1$, respectively (*cf.* Figure 4). The half-band widths, frequencies, and intensities of these overtones are given in Table III. For 488.0 nm excitation, presumably on account of its better signal/noise ratio, overtone progressions out to $13\nu_1$ were observed for cyclohexane solutions of titanium tetraiodide (Figure 5). With 457.9 nm excitation the

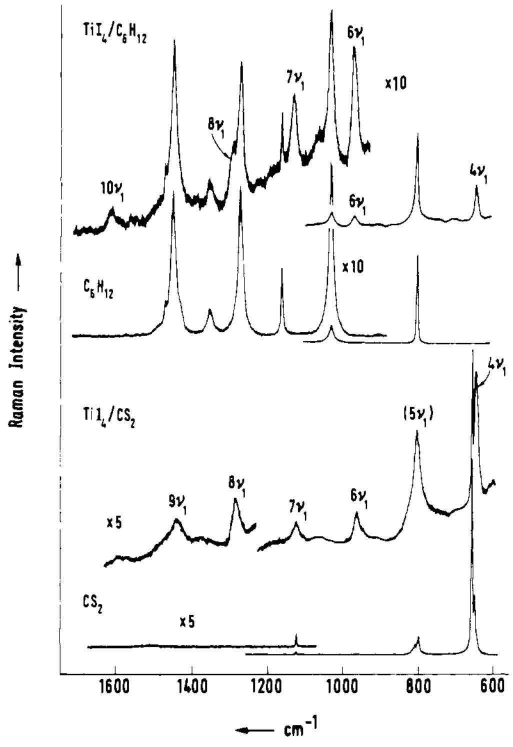

Figure 4. Resonance Raman spectrum of titanium tetraiodide in cyclohexane and in carbon disulfide solutions obtained by use of 514.5 nm excitation. For the cyclohexane solution, the instrumental settings were slit widths 150/200/150 μ, gain 20K (inset 2K), tc 2 sec, scanning speed 10 cm^{-1}/min. For the carbon disulfide spectrum, the settings were the same except for the gain 10K (inset 2K). The solvent spectra were run at similar settings in each case. Overtones are marked as $n\nu_1$.

Table III. $\nu_1(a_1)$ Fundamental Frequency and Overtones of Titanium Tetraiodide Using 488.0 and 514.5 nm Excitation

	Frequency, cm^{-1}				$\Delta\nu_{1/2}$, cm^{-1}	
Band	C_6H_{12} soln[a]	CCl_4 soln	CS_2 soln	Solid	C_6H_{12}	Solid
ν_1	161.2$_5$	160.5	160.1	160.8	4.5	4.5
ν_3 $2\nu_1$	322.2	322.7	319.4	321.4	6	5
$3\nu_1$	483.0	484.1	480.1	481.4	8	5.8
$4\nu_1$	643.9	645.8	641.8	641.5	10	6.6
$5\nu_1$	804		801.5	801.4	12.5	7.5
$6\nu_1$	965	968	962	960.5	16	8.6
$7\nu_1$	1124		1121	1121.5	19	10
$8\nu_1$	1285		1283	1279.5	23	12
$9\nu_1$	1446		1441	1439		15
$10\nu_1$	1607			1598.5	28	17
$11\nu_1$	1766			1758.5		20
$12\nu_1$	1925			1917		25
$13\nu_1$	2084					

[a] With 514.5 nm excitation, the depolarization ratios of ν_1, $\nu_3/2\nu_1$, $3\nu_1$, and $4\nu_1$ were found to have upper limits of 0.02, 0.06, 0.03, and 0.05, respectively.

Raman spectrum of the molecule reverts to normal as the resonance situation is now lost.

It is noteworthy that, in agreement with the theory of Nafie, *et al.*,[19] it is only the totally symmetric fundamental which displays the RRE. Moreover, experiment clearly showed that there is an optimum concentration for the RRE; if the concentration is too high the solution becomes so absorbing that no spectra

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(18) This same observation, although for fewer overtones, has recently been reported for carbon disulfide and benzene solutions by T. Kamasuki and S. Maed, *Chem. Phys. Lett.*, **19**, 379 (1973).

(19) L. A. Nafie, P. Stein, and W. L. Peticolas, *Chem. Phys. Lett.*, **12**, 131 (1971).

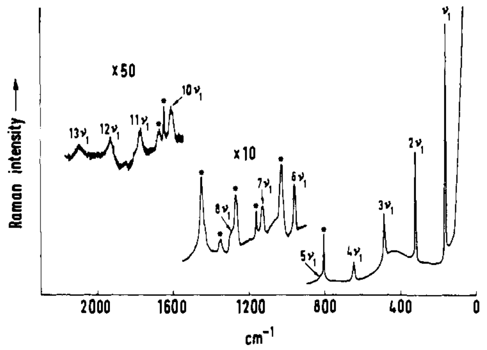

Figure 5. Resonance Raman spectrum of titanium tetraiodide in cyclohexane obtained with 488.0 nm excitation. Slit widths 180/300/180 μ, gain 50K/5K/1K, tc 0.4 sec, scanning speed 10 cm^{-1}/min.

could be observed at all. This optimum concentration appears to be *ca.* 10^{-2} *M*, at which concentration the resonance Raman spectrum of titanium tetraiodide largely swamps the nonresonance Raman spectrum of the solvent.

The overtones display the following characteristic features of the RRE, as distinct from resonance fluorescence:[10] (a) continuous increase in half-band width (Figure 6) and continuous decrease in peak height and peak area as the vibrational quantum number (n) increases and (b) all overtones are polarized to the same extent as the fundamental (Table III). Similar effects have been observed previously for the resonance Raman spectra of the permanganate and chromate ions.[20] The increase in half-band width with n is attributed in part to anharmonicity in the vibrational potential[21] and in part to environmental effects (note that $\Delta\nu_{1/2}$ for the solid is less than that for cyclohexane solutions (*cf.* Figure 6 and Table III)).

The observation of a large number of overtones of $\nu_1(a_1)$ in the RRE for titanium tetraiodide makes it possible to determine accurately the anharmonicity constant X_{11} and the harmonic frequency ω_1 of this molecule. The observed wave number $\nu(n)$ of any overtone of an anharmonic oscillator is given by[22]

$$\begin{aligned}\nu(n) &= G(n) - G(0)\\ &= n\omega_1 - X_{11}(n^2 + n) + \ldots\end{aligned}$$

where $G(n)$ is the term value of the nth eigenvalue and n is the vibrational quantum number. X_{11} and ω_1 may therefore be determined from a plot of $\nu(n)/n$ *vs.* n (Figure 7). The results, both for titanium tetraiodide in the solid state as well as in cyclohexane solution, are given in Table IV, together with corresponding results for the permanganate and chromate ions likewise obtained by way of the RRE.[20] The highly harmonic nature of the $\nu_1(a_1)$ fundamental is presumably a consequence of the fact that even the frequency $13\nu_1$ is very near the bottom of the appropriate potential well, and far removed from the likely dissociation energy of the molecule.

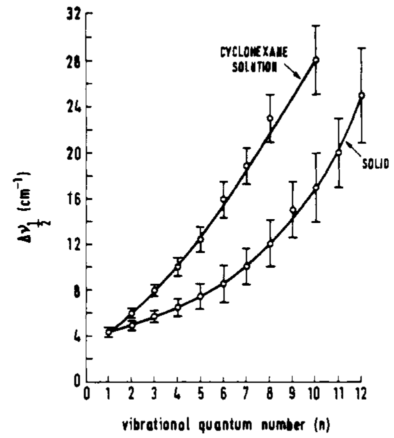

Figure 6. The observed half-band widths for the $\nu_1(a_1)$ fundamental and its overtones of titanium tetraiodide in cyclohexane.

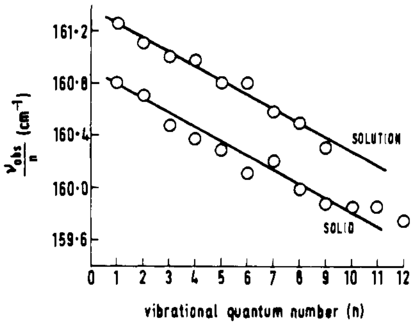

Figure 7. Plot of $\nu(n)/n$ *vs.* n to determine the anharmonicity constant X_{11} and ω_1 of titanium tetraiodide, both in the solid state and in cyclohexane.

Table IV. Harmonic Frequencies and Anharmonicity Constants of Some Tetrahedral Species

Species	State	ν_0, cm^{-1} [a]	ω_1, cm^{-1}	X_{11}, cm^{-1}
TiI_4	Solid	19,435	161.0 ± 0.2	0.11 ± 0.03
TiI_4	C_6H_{12} soln	19,435	161.5 ± 0.2	0.11 ± 0.03
$KMnO_4$ [b]	Solid	19,435	845.5 ± 0.5	1.1 ± 0.2
MnO_4^- [b]	H_2O soln	20,492	839.5 ± 0.5	1.0 ± 0.2
K_2CrO_4 [b]	Solid	27,487	854.4 ± 0.5	0.71 ± 0.1

[a] ν_0 is the excitation frequency. [b] Reference 20.

Overtone Intensities. The intensities of the observed overtones and their number reach a maximum for the 488.0 and 514.5 nm exciting lines, *i.e.*, the lines which correspond most closely with the first allowed electronic transition of titanium tetraiodide (Table V).

Recent theoretical work[19] has indicated the following relationship between the relative intensities (R_n) of overtones

$$R_n = I_n/I_1 = \frac{1}{2}ns\left[\frac{(2\omega)^2 - \Gamma_\alpha^2}{(n\omega)^2 - \Gamma_\alpha^2}\right]R_2R_{n-1}$$

where

$$s = \left[\left(\frac{\omega_1 - n\omega}{\omega_1 - (n-1)\omega}\right)\left(\frac{\omega_1 - \omega}{\omega_1 - 2\omega}\right)\right]^4$$

ω_1 is the exciting frequency (cm^{-1}), ω is the frequency of the fundamental (cm^{-1}), and Γ_α is the damping term, introduced so that the intensity at resonance does not go to infinity.

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(20) W. Kiefer and H. J. Bernstein, *Mol. Phys.*, **23**, 835 (1972).

(21) The broadening of the overtone bands arises from cross-terms in the anharmonic constants and the fact that the fundamentals have such low frequencies that ν_2, ν_3, and ν_4 are very significantly populated to high n. Thus

$$G(n,m,p,q) - G(0,m,p,q) = n\omega_1 - (n^2 + n)X_{11} - n[X_{12}(m + 1/2) + X_{13}(p + 1/2) + X_{14}(q + 1/2)]$$

Terms such as $X_{12}(m + 1/2)$ therefore contribute to the breadth in a way proportional to n.

(22) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1945, p 205.

Table V. Relative Intensities of the $\nu_1(a_1)$ Fundamental and Its Overtones for Titanium Tetraiodide in Cyclohexane at Different Exciting Wavelengths (corrected for spectral response)

	Wavelength, nm								
Band	482.5	488.0	514.5	520.8	568.2	598.3	622.4	647.1	Calcd[a]
ν_1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
$\nu_3/2\nu_1$	0.52	0.64	0.67	0.57	0.44	0.38	0.29	0.27	0.67
$3\nu_1$	0.27	0.27	0.41	0.36	0.14				0.41
$4\nu_1$	0.16	0.17	0.21	0.26	0.05				0.17
$5\nu_1$		0.104	0.15	*b*					0.060
$6\nu_1$		0.054	0.081	0.13					0.018
$7\nu_1$		0.038	0.054	0.095					0.005
$8\nu_1$		0.033	0.039						0.001
$9\nu_1$		*b*	*b*						
$10\nu_1$		0.013	0.021						
$11\nu_1$		0.011							
$12\nu_1$		0.007							
$13\nu_1$		0.004							

[a] See text; the results are based on a damping term of 196 cm^{-1}. [b] Intensity could not be determined owing to overlap with a solvent peak.

The value of the damping term may be established by using the experimental values of R_2 and R_3 in the equation. Then values for R_4, etc., may be calculated and compared with those found experimentally. This calculation has been carried through using the data obtained for titanium tetraiodide in cyclohexane at 514.5 nm excitation, and the results are included in the final column of Table V (the calculated value of Γ_α was 196 cm^{-1}). The calculated intensities of the higher overtones fall faster than is found experimentally, in exactly the same manner as reported and discussed for the higher overtones of iodine.[19]

The fundamental $\nu_3(t_2)$ is virtually coincident with $2\nu_1$ and thus in order to determine the manner in which the intensity ratio $I(2\nu_1)/I(\nu_1)$ varies with the exciting wavelength, the contribution made by $\nu_3(t_2)$ to the overtone band must be subtracted. The results are given in Table VI, from which it is clear that the ratio $I(2\nu_1)/I(\nu_1)$ increases steadily with the extinction coefficient of the first allowed electronic transition of the molecule; *i.e.*, the intensity of the first overtone relative to that of the fundamental increases as ν_0 approaches ν_e.

Table VI. Intensity of the First Overtone of $\nu_1(a_1)$ of Titanium Tetraiodide Relative to That of the Fundamental as a Function of Exciting Wavelength

Wavelength of exciting line, nm	$I(\nu_3/2\nu_1)/I(\nu_1)$	ρ	$I(2\nu_1)/I(\nu_1)$[a]	ϵ
647.1	0.27	0.62	0.047	0
622.4	0.29	0.55	0.077	45
598.3	0.38	0.55	0.10	250
568.2	0.44	0.47	0.16	1100
520.8	0.57	0.08	0.51	5200
514.5	0.67	0.06	0.61	5400
488.0	0.64	0.05	0.60	2700
482.5	0.52	0.08	0.46	2100

[a] Based on ν_3 being depolarized with ρ = 0.75, and $2\nu_1$ being polarized with ρ = 0.

Molecular and Bond Polarizability Derivatives. The intensity of the $\nu_1(a_1)$ fundamental of titanium tetraiodide has been measured relative to that of the usual internal standard, the $\nu_1(a_1)$ fundamental of carbon tetrachloride, by use of the 647.1, 568.2, 514.5, and 488.0 nm exciting lines. All apparent relative intensities were corrected to true relative intensities by means of the spectral response curve for the instrument. The true relative intensities at each exciting frequency have been converted to bond polarizability derivatives by use of the relationships in Table VII and the value[23] $\bar{\alpha}'_{\mathrm{CCl}}$ = 2.04 Å^2. The results given in Table VII indicate the strong dependence of $\bar{\alpha}'_{\mathrm{TiI}}$ on $\nu_0 - \nu_e$, and confirm that the titanium–iodine bond polarizability derivative (estimated to be 13 Å^2 at zero exciting frequency) is the highest known for a formal single bond.

Table VII. Molar Intensity of the $\nu_1(a_1)$ Fundamental of Titanium Tetraiodide Relative to That of the $\nu_1(a_1)$ Band of Carbon Tetrachloride

Exciting line, nm	I_2M_1/I_1M_2	f	$\bar{\alpha}'_{\mathrm{TiI}}$, Å^2
647.1	110	5.086	18.0
568.2	480	5.036	37.7
514.5	2550	5.003	87
488.0	2360	4.987	84

$$f = \left[\frac{\nu_0 - \Delta\nu_2}{\nu_0 - \Delta\nu_1}\right]^4 \left[\frac{\Delta\nu_1}{\Delta\nu_2}\right] \left[\frac{1 - \exp(-hc\Delta\nu_1/kT)}{1 - \exp(-hc\Delta\nu_2/kT)}\right]$$

$$\frac{I_2M_1}{I_1M_2} = f\left(\frac{\bar{\alpha}'_2}{\bar{\alpha}'_1}\right)^2$$

$$\left(\frac{\bar{\alpha}'_2}{\bar{\alpha}'_1}\right) = \left(\frac{\mu_2}{\mu_1}\right)^{1/2}\left(\frac{\bar{\alpha}'_{\mathrm{TiI}}}{\bar{\alpha}'_{\mathrm{CCl}}}\right)^a$$

[a] μ is the reduced mass.

Acknowledgment. We are grateful to the S. R. C. for financial support and to Coherent Radiation (U. K.) Ltd. for the loan of a tunable dye laser.

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