

Contribution from The Christopher Ingold Laboratories,
University College London, London WC1H 0AJ, England

Raman and Resonance Raman Spectroscopic Studies on the Tetraiodides of Carbon, Silicon, Germanium, and Tin Using Visible and Ultraviolet Exciting Lines

ROBIN J. H. CLARK* and TREVOR J. DINES

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The resonance Raman spectra of GeI_4 and SnI_4 in cyclohexane, obtained with UV excitation, display a progression in the totally symmetric stretching mode (ν_1) extending to $7\nu_1$ and $15\nu_1$, respectively. These data lead to harmonic wavenumbers (ω_1) of 158.9 and 151.2 cm^{-1} for GeI_4 and SnI_4 , respectively, and to anharmonicity constants (x_{11}) of -0.09 and -0.02 cm^{-1} , respectively. The preresonance behavior of Cl_4 and SiI_4 has also been studied. All of the tetraiodides are susceptible to photodecomposition, especially with UV excitation. The results are discussed in terms of current theories of the resonance Raman effect.

Introduction

In previous studies carried out in this laboratory^{1,2} the Raman intensities of all four bands attributed to the fundamentals of SiI_4 , GeI_4 , and SnI_4 were determined for cyclohexane solutions. In another study 363.8-nm excitation³ was used to record the resonance Raman spectrum of SnI_4 in cyclohexane solution, on a spectrometer which had poor sensitivity in the ultraviolet (UV) region.

In the present study we have used a spectrometer incorporating UV optics and UV excitation from a powerful argon ion laser to record the resonance Raman spectra of GeI_4 and SnI_4 in cyclohexane solutions. We have also investigated the preresonance behavior both of Cl_4 in a CsI disk at low temperature by using the deep red lines of a krypton ion laser and of SiI_4 in cyclohexane solution by using visible and UV argon ion laser excitation. Cyclohexane was chosen as solvent for two reasons: (1) its virtual lack of interaction with group 4 tetraiodides, therefore enabling the measurement of frequency data which are close to the gas-phase values; (2) the absence of any measurable preresonance effects with visible and near-UV excitation, permitting its Raman bands to be used as internal intensity standards.

Theory

For a Raman transition between two states i and f of a scattering molecule the intensity of light scattered at 90° to the direction of illumination is given by

$$I = \frac{\pi^2(\bar{\nu}_0 \pm \bar{\nu}_{fi})^4 I_0 \sum_{\rho\sigma} |(\alpha_{\rho\sigma})_{fi}|^2}{\epsilon_0^2 [1 - \exp(-hc\bar{\nu}_{fi}/kT)]} \quad (1)$$

where I_0 is the irradiance (W m^{-2}) of the incident radiation of wavenumber $\bar{\nu}_0$, $\bar{\nu}_{fi}$ is the wavenumber associated with the Raman transition $f \leftarrow i$, h is Planck's constant, c is the velocity of light, ϵ_0 is the permittivity of free space, k is the Boltzmann constant, T is the temperature, and $(\alpha_{\rho\sigma})_{fi}$ is the $\rho\sigma$ th element of the transition polarizability tensor. Following Albrecht's theory of resonance Raman scattering⁴

$$(\alpha_{\rho\sigma})_{fi} = A + B \quad (2)$$

where

$$A = (hc)^{-1} (\mu_{\rho}^0)_{ge} (\mu_{\sigma}^0)_{eg} \sum_v \frac{\langle f|v\rangle \langle v|i\rangle}{\bar{\nu}_{ev} - \bar{\nu}_0 + i\Gamma_{ev}} \quad (3)$$

and

$$B = (hc)^{-1} (\mu_{\rho}^0)_{ge} \left(\frac{\partial \mu_{\sigma}}{\partial Q} \right)_{eg}^0 \sum_v \frac{\langle f|v\rangle \langle v|Q|i\rangle}{\bar{\nu}_{ev} - \bar{\nu}_0 + i\Gamma_{ev}} + (hc)^{-1} \left(\frac{\partial \mu_{\rho}}{\partial Q} \right)_{ge}^0 (\mu_{\sigma}^0)_{eg} \sum_v \frac{\langle f|Q|v\rangle \langle v|i\rangle}{\bar{\nu}_{ev} - \bar{\nu}_0 + i\Gamma_{ev}} \quad (4)$$

where $(\mu_{\rho}^0)_{ge}$ is the transition dipole moment in the ρ direction associated with the transition $g \leftarrow e$ and $(\partial \mu_{\rho} / \partial Q)_{ge}^0$ is its first derivative with respect to a normal coordinate Q . The zero superscript refers to the equilibrium configuration of the molecule. $\bar{\nu}_{ev}$ is the wavenumber associated with the transition $ev \leftarrow gi$, where v is the vibrational level in the excited state e , and $i\Gamma_{ev}$ is a complex damping constant related to the full width half-maximum (fwhm) of the absorption band arising from this transition.

As a general rule A -term scattering is exhibited only by totally symmetric modes (although it may arise from certain nontotally symmetric modes as a consequence of Jahn-Teller coupling in a degenerate excited state; see below); this is because it is only these modes which alter the equilibrium nuclear positions and hence give rise to nonzero Franck-Condon overlap factors $\langle f|v\rangle \langle v|i\rangle$. In molecules with more than one totally symmetric mode the one that is most resonance enhanced is that along whose normal coordinate the greatest displacement occurs in the resonant electronic transition. For the group 4 tetraiodides, however, which have T_d symmetry, there is only one totally symmetric mode, ν_1 , and this mode may be resonance enhanced due to a distortion along Q_1 in the resonant electronic transition $T_2 \leftarrow A_1$, which is of $\pi^* \leftarrow n$ character.

The dominant feature of A -term scattering is a long overtone progression in the totally symmetric fundamental with a decrease in intensity and increase in fwhm for successive overtones. Measurement of the wavenumber values of the fundamental and its overtones enables the determination of the harmonic wavenumber ω_1 and the anharmonicity constant x_{11} from a plot of $v_1\nu_1/v_1$ vs. v_1 , which should be a straight line of gradient x_{11} and (to a first approximation) intercept $\omega_1 + x_{11}$.

The electronic spectra of the group 4 tetraiodides show no vibrational structure at room temperature and we may therefore conclude that the fwhm's of the vibrational sublevels are greater than the vibrational interval in the excited state. The excitation profile of ν_1 should therefore peak at or close to the position of the $\pi^* \leftarrow n$ band maximum in the absorption spectrum, i.e., the Franck-Condon maximum.

- (1) R. J. H. Clark and C. J. Willis, *Inorg. Chem.*, **10**, 1118 (1971).
- (2) R. J. H. Clark and P. D. Mitchell, *J. Mol. Spectrosc.*, **51**, 458 (1974).
- (3) R. J. H. Clark and P. D. Mitchell, *J. Chem. Soc., Chem. Commun.*, 762 (1973).
- (4) J. Tang and A. C. Albrecht, *Raman Spectrosc.*, **2**, 33 (1970).

Table I. Details of the Electronic Absorption Spectra of the Group 4 Tetraiodides

compd	state	λ_{\max}/nm	$\tilde{\nu}_{\max}/\text{cm}^{-1}$
Cl_4^a	isooctane soln	383.0	26 110
		302.0	33 110
SiI_4^b	cyclohexane soln	285.4	35 040
GeI_4^c	cyclohexane soln	360.4	27 750
		317.0	31 550
		364.5	27 435
SnI_4^c	cyclohexane soln	285.7	35 000

^a M. Ito, P.-K. Huang, and E. Kosower, *Trans. Faraday Soc.*, **57**, 1662 (1961). ^b Reference 2. ^c Present work.

In the Herzberg-Teller approximation the term $(\partial\mu_p/\partial Q)_{ge}^0$ is given by $\sum_s[(\mu_p)_{gs}^0 h_{es}^Q]/[hc(\tilde{\nu}_s - \tilde{\nu}_e)]$, where s is a higher excited state and the term h_{es}^Q is the vibronic coupling integral $\langle s|\partial H/\partial Q|e\rangle$. Then, for a single state s

$$B = (hc)^{-2}(\mu_p)_{ge}^0(\mu_p)_{gs}^0 h_{es}^Q(\tilde{\nu}_s - \tilde{\nu}_e)^{-1} \sum_v \frac{\langle f|v\rangle \langle v|Q|i\rangle}{\tilde{\nu}_{ev} - \tilde{\nu}_0 + i\Gamma_{ev}} + (hc)^{-2}(\mu_p)_{gs}^0(\mu_p)_{eg}^0 h_{es}^Q(\tilde{\nu}_s - \tilde{\nu}_e)^{-1} \sum_v \frac{\langle f|Q|v\rangle \langle v|i\rangle}{\tilde{\nu}_{ev} - \tilde{\nu}_0 + i\Gamma_{ev}} \quad (5)$$

The integral h_{es}^Q is nonvanishing for a vibration whose irreducible representation is contained in the direct product of the irreducible representations of the two electronic transitions $e \leftarrow g$ and $s \leftarrow g$. For T_d symmetry, only electronic transitions of T_2 symmetry are dipole allowed and the direct product of T_2 with itself is $A_1 + E + T_1 + T_2$. It follows then, that for the group 4 tetraiodides any one of the vibrational modes can participate in the vibronic coupling of a pair of electronic transitions, with concomitant enhancement of intensity, the mode which is most effective in mixing the two excited electronic states having the greatest enhancement. B -Term enhancement is, however, usually smaller than A -term enhancement due to the additional factors h_{es}^Q and $(\tilde{\nu}_s - \tilde{\nu}_e)^{-1}$.

Nontotally symmetric vibrations may also be resonance enhanced by vibronic coupling within a degenerate excited state.⁵ Such a vibronic coupling gives rise to a distortion of the equilibrium configuration of the molecule in the excited state (Jahn-Teller distortion). The Jahn-Teller-active modes are those contained in the symmetric direct product of the irreducible representation of the degenerate excited state with itself. It follows then that for the group 4 tetraiodides any of the three nontotally symmetric modes may be Jahn-Teller active in the T_2 excited state. The effect may be manifested in the Raman spectrum in two ways: (1) an A -term enhancement of the band attributable to the nontotally symmetric fundamental as resonance is approached, with the possible appearance of an overtone progression under rigorous resonance conditions; (2) the appearance of an overtone progression in the totally symmetric mode based on a single quantum of the nontotally symmetric fundamental under rigorous resonance conditions.

Experimental Section

The rotating-cell technique⁶ was used to measure the Raman spectra of SiI_4 , GeI_4 , and SnI_4 as 10^{-2} - 10^{-3} M solutions in cyclohexane. Decomposition was minimized by subliming the iodides in vacuo; the solvent was carefully dried over CaH_2 , thoroughly degassed, and distilled into the sample cell, which was subsequently sealed off under vacuum. The low-temperature Raman spectrum of Cl_4 in a CsI disk was recorded at ca. 100 K in a liquid nitrogen cold cell described elsewhere.⁷ The laser beam was swept over the surface of the sample by inserting a rapidly rotating glass block between the focusing lens and the sample, in an endeavor to minimize thermal and photochemical decomposition of the sample.

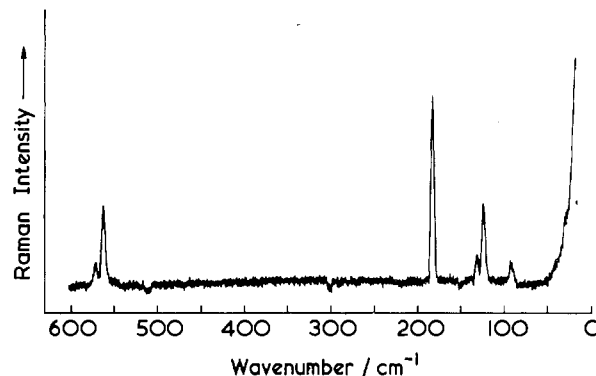


Figure 1. Raman spectrum of Cl_4 in a CsI disk at ca. 100 K (λ_0 647.1 nm, power 200 mW, gain 10^4 counts s^{-1} , integration time 0.5 s, time constant 1.0 s, spectral slit width 4.5 cm^{-1} , scan speed $0.2 \text{ cm}^{-1} \text{ s}^{-1}$).

Table II. Wavenumbers and Assignments of the Bands in the Raman Spectrum of Carbon Tetraiodide at 100 K

assignt	$\tilde{\nu}/\text{cm}^{-1}$ ^a	$\tilde{\nu}/\text{cm}^{-1}$ ^b	assignt	$\tilde{\nu}/\text{cm}^{-1}$ ^a	$\tilde{\nu}/\text{cm}^{-1}$ ^b
$\nu_2(e)$	89.3	90	$\nu_1(a_1)$	180.5	178
$\nu_4(t_2)$	122.7	123	$\nu_3(t_2)$	560.5	555 ^c
	130.0			570.5	

^a Present work, $\pm 0.5 \text{ cm}^{-1}$. ^b Reference 10. ^c Value obtained from an infrared band measurement.

Table III. Intensity Measurements on ν_1 of Carbon Tetraiodide as a CsI Disk at ca. 100 K^a

λ_0/nm	$\tilde{\nu}_0/\text{cm}^{-1}$	intens	λ_0/nm	$\tilde{\nu}_0/\text{cm}^{-1}$	intens
752.5	13 289	1.0	647.1	15 453	4.3
676.4	14 784	2.6			

^a Normalized to unity at 752.5 nm.

A Spex Ramalog 6 double monochromator with 1800 line/mm holographic gratings, in conjunction with Coherent Radiation Model 52 Kr^+ and Model 12 Ar^+ ion lasers, was used to record the Raman spectra. For visible exciting lines spectral purity of the laser beam was achieved by insertion of a Claassen filter⁸ before the focusing lens. In the UV region a Pellin-Broca prism⁹ was used.

Detection was by standard photon counting techniques; an RCA C31034 photomultiplier with a Spex DPC-2 digital photon counter was employed. For some of the work on Cl_4 a Spex 1401 double monochromator was used because of its greater efficiency in the deep red region. All frequency measurements were calibrated by using the emission spectrum of neon, and band intensities were corrected for the spectral response of the instrument.

The electronic spectroscopic data for GeI_4 and SnI_4 in cyclohexane solution were recorded on a Cary 14 spectrophotometer.

Results and Discussion

(a) **Carbon Tetraiodide.** The only previous Raman spectroscopic study of Cl_4 is that reported by Stammreich et al.¹⁰ in which the 667.82-nm line of a helium lamp was used as an excitation source. They found that, even at this (comparatively) long wavelength, rapid photochemical decomposition of Cl_4 to I_2 and other products took place but that crystals suspended in glycerol gave satisfactory spectra for several hours. In the present study photochemical decomposition was reduced by recording the Raman spectrum of Cl_4 in a CsI disk held at ca. 100 K. The spectrum shown in Figure 1 was recorded with 647.1-nm excitation. With this line the sample endured for a number of hours but not at shorter wavelengths; in fact with excitation wavelengths shorter than 568.2 nm no spectrum could be obtained.

(5) M. Tsuboi and A. Y. Hirakawa, *J. Mol. Spectrosc.*, **56**, 146 (1975).
 (6) R. J. H. Clark, *Adv. Infrared Raman Spectrosc.*, **1**, 143 (1975).
 (7) R. J. H. Clark and P. C. Turtle, *Inorg. Chem.*, **17**, 2526 (1978).

(8) H. Claassen, H. Selig, and J. Shamir, *Appl. Spectrosc.*, **23**, 8 (1969).
 (9) P. Pellin and A. Broca, *J. Phys. (Paris)*, **8**, 314 (1899).
 (10) H. Stammreich, Y. Tavares, and D. Bassi, *Spectrochim. Acta*, **17**, 661 (1961).

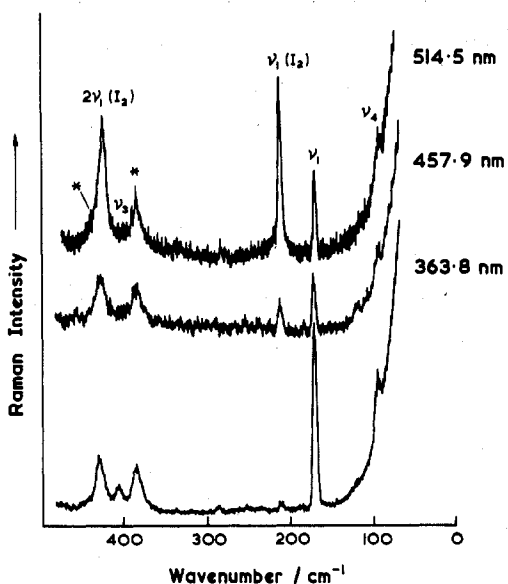


Figure 2. Preresonance Raman spectra of SiI_4 in cyclohexane solution (λ_0 363.8, 457.9, and 514.5 nm; power 200 mW; gain 5×10^4 , 2×10^3 , and 5×10^3 counts s^{-1} , respectively; integration time = time constant = 0.2 s; scan speed $1.0 \text{ cm}^{-1} \text{ s}^{-1}$; spectral slit width 10, 6, and 5 cm^{-1} , respectively). The asterisk indicates a cyclohexane band.

Table IV. Wavenumbers and Assignments of the Bands in the Raman Spectrum of Silicon Tetraiodide in Cyclohexane Solution

assignt	$\tilde{\nu}/\text{cm}^{-1}$ ^a	$\tilde{\nu}/\text{cm}^{-1}$ ^b	assignt	$\tilde{\nu}/\text{cm}^{-1}$ ^a	$\tilde{\nu}/\text{cm}^{-1}$ ^b
$\nu_2(\text{e})$		62	$\nu_1(\text{a}_1)$	168.1 ± 0.5	170
$\nu_4(\text{t}_2)$	90.5 ± 0.5	92	$\nu_3(\text{t}_2)$	405.5 ± 2	406

^a Present work. ^b Reference 1.

All of the Cl_4 fundamentals were observed and the wavenumber values are given in Table II, together with those obtained by Stammreich et al. Splitting of the bands assigned to the triply degenerate modes was observed in the present study (7.3 cm^{-1} for ν_4 and 10.0 cm^{-1} for ν_3) but not by Stammreich et al., although they observed a 4-cm^{-1} splitting in ν_4 in the infrared spectrum. This may be due to better resolution in our spectrum or it may reflect a different crystal structure for Cl_4 at 100 K from that at room temperature.

The Raman intensity of ν_1 was measured, with ν_1 of K_2SO_4 as an internal intensity standard, for 647.1-, 676.4-, and 752.5-nm Kr^+ excitation (lower wavelength lines caused photochemical decomposition), and the data are presented in Table III. There is evidence for A -term enhancement of ν_1 as the lowest dipole-allowed transition is approached. An attempt to measure the Raman intensities of Cl_4 in cyclohexane solution was frustrated by rapid decomposition.

(b) Silicon Tetraiodide. The 514.5-, 457.9-, and 363.8-nm Ar^+ excitations were used to record the Raman spectrum of SiI_4 in cyclohexane solution. Considerable photochemical decomposition resulted with excitation in the UV region, I_2 being produced. The spectra are shown in Figure 2 and the wavenumber values are given in Table IV. It can be seen that the resonance Raman spectrum of I_2 is very much in evidence with 514.5-nm excitation (which is close to the absorption maximum of I_2), but much less intense with the shorter wavelength exciting lines (which are off-resonance for I_2).

An attempt to measure the frequency dependence of the Raman intensities was seriously hampered by the photochemical decomposition of SiI_4 ; it was noted that the increase in intensity on going from 514.5- to 363.8-nm excitation was by a factor of 2.5 for ν_1 (after correction for the $\tilde{\nu}^4$ dependence) and ca. 1.5 for ν_3 . The enhancement of the intensity of ν_1 is almost certainly due to A -term scattering from the lowest

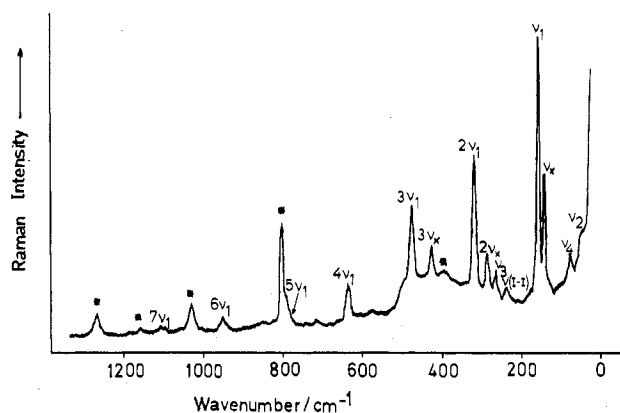


Figure 3. Resonance Raman spectrum of GeI_4 in cyclohexane solution (λ_0 363.8 nm, power 200 mW, gain 10^4 counts s^{-1} , integration time 0.5 s, time constant 1.0 s, scan speed $0.5 \text{ cm}^{-1} \text{ s}^{-1}$, spectral slit width 5 cm^{-1}). The asterisk indicates a cyclohexane band.

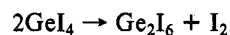
Table V. Wavenumbers and Assignments of the Bands in the Resonance Raman Spectrum of Germanium Tetraiodide in Cyclohexane Solution

assignt	$\tilde{\nu}/\text{cm}^{-1}$	assignt	$\tilde{\nu}/\text{cm}^{-1}$
$\nu_2(\text{e})$	~ 60	$2\nu_1(\text{A}_1)$	317.5 ± 0.5
$\nu_4(\text{t}_2)$	79.0 ± 2	$3\nu_x$	427.6 ± 0.5
$\nu_x, \nu_{\text{sym}}(\text{GeI})/\text{Ge}_2\text{I}_6?$	142.5 ± 0.5	$3\nu_1(\text{A}_1)$	475.3 ± 0.5
$\nu_1(\text{a}_1)$	158.7 ± 0.5	$4\nu_1(\text{A}_1)$	633.4 ± 0.5
$\nu(\text{I-I})$	213.0 ± 0.5	$5\nu_1(\text{A}_1)$	~ 795
$\nu_3(\text{t}_2)$	264.1 ± 0.5	$6\nu_1(\text{A}_1)$	949.2 ± 0.8
$2\nu_x$	285.6 ± 0.5	$7\nu_1(\text{A}_1)$	1107 ± 1

dipole-allowed transition at 35000 cm^{-1} , whereas that of ν_3 is less certain. It may be due to B -term scattering arising from the vibronic coupling of the two lowest excited states or to A -term scattering arising from Jahn-Teller coupling in the triply degenerate excited state at 35000 cm^{-1} . The latter is more likely in that we would expect the degree of intensity enhancement to be much less for B -term scattering. The relative enhancements of the intensities of ν_1 and ν_3 could be interpreted as a difference in the displacement of the molecular geometry along Q_1 and Q_3 in the resonant electronic transition.

(c) Germanium Tetraiodide. The resonance Raman spectrum of GeI_4 , recorded with 363.8-nm excitation, is shown in Figure 3 and the wavenumber values are given in Table V. The outstanding feature of the spectrum is an overtone progression in ν_1 extending to $7\nu_1$. Higher overtones may be present but they would be obscured by solvent bands, as is $5\nu_1$. Seven other bands were observed which are not attributable to the solvent; three of these could be assigned to the nontotally symmetric fundamentals of GeI_4 , the two low-lying deformation modes being observed as weak shoulders on the Rayleigh line. The other four bands could not be assigned to GeI_4 and therefore arise from impurities. It was observed that on exposure to the UV laser beam the sample gradually darkened from yellow to opaque red. This was believed to be due to the liberation of I_2 and the band at 213 cm^{-1} is assigned to $\nu(\text{I-I})$. It was found that when the Raman spectrum of GeI_4 was recorded with 514.5-nm excitation prior to UV exposure, no impurity bands could be detected, but immediately after UV exposure both $\nu(\text{I-I})$ and the impurity band at 142.5 cm^{-1} could be observed. On removal from UV irradiation the solution returned to its original color over a period of hours and the impurity bands could no longer be detected in the 514.5 nm excited Raman spectrum after 20 h.

A reasonable assignment for the 142.5-cm^{-1} band would be to the totally symmetric Ge-I stretching mode of the hitherto unknown Ge_2I_6 , generated photochemically by the reaction



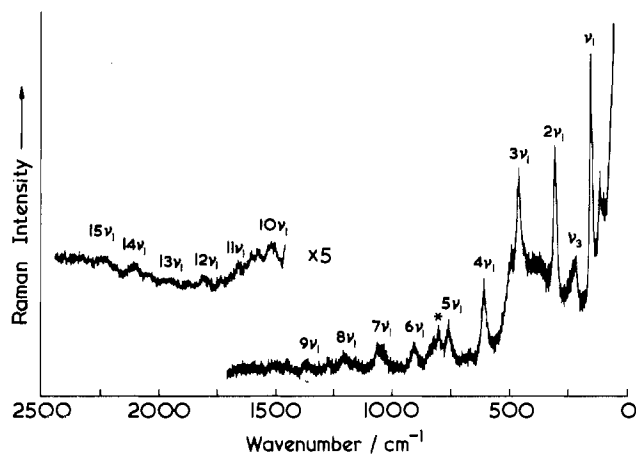


Figure 4. Resonance Raman spectrum of SnI_4 in cyclohexane solution (λ_0 363.8 nm, power 200 mW, gain 10^4 counts s^{-1} , integration time = time constant = 0.1 s, scan speed $1.0 \text{ cm}^{-1} \text{ s}^{-1}$, spectral slit width 10 cm^{-1} ; for inset, gain 2×10^3 counts s^{-1} , integration time 0.5 s, time constant 1.0 s, scan speed $0.5 \text{ cm}^{-1} \text{ s}^{-1}$).

Such an assignment is consistent with the following facts:

1. The wavenumber of the totally symmetric Si-I stretching mode of Si_2I_6 (154 cm^{-1}) is less than that of SiI_4 (168.1 cm^{-1}).

2. The band at 213 cm^{-1} attributed to I_2 is generated simultaneously with the 142.5-cm^{-1} band on UV excitation of GeI_4 , as required by the above equation, and likewise disappears with it at the same rate (half-life = 20 min) on removal of the UV excitation.

3. Overtones of the 142.5-cm^{-1} band appear at 285.6 and 427.6 cm^{-1} , consistent with resonance enhancement of a totally symmetric stretching mode, with 363.8-nm excitation.

4. Such a mode is expected to be a Ge-I stretching coordinate, since the $\pi^* \leftarrow n$ electronic bands of Ge_2I_6 must be very close in wavenumber to those of GeI_4 .

5. The depolarization ratio (ρ_1) of the 142.5-cm^{-1} band was found to be 0.31 ± 0.03 . This is consistent with the value of $1/3$ required for a totally symmetric mode with excitation in resonance with a nondegenerate electronic transition of a molecule with D_{3d} symmetry.¹²

Since the intensities of the bands attributed to Ge_2I_6 do not increase progressively with UV irradiation, it appears that a steady-state situation is set up. The photochemical decomposition of the sample, with concomitant liberation of I_2 , did not impair the quality of the observed resonance Raman spectrum but did preclude the collection of reliable intensity data in the UV region and so we were unable to construct excitation profiles for GeI_4 .

From the overtone progression in ν_1 it was possible to compute values for the harmonic wavenumber ω_1 and the anharmonicity constant x_{11} , the results being $\omega_1 = 158.9 \pm 0.1 \text{ cm}^{-1}$ and $x_{11} = -0.09 \pm 0.02 \text{ cm}^{-1}$.

(d) Tin Tetraiodide. The resonance Raman spectrum of SnI_4 , recorded with 363.8-nm excitation, is shown in Figure 4 and the wavenumber values, together with those obtained by Clark and Mitchell,³ are given in Table VI. Its most outstanding feature is a progression in ν_1 extending to $15\nu_1$, from which it was determined that $\omega_1 = 151.2 \pm 0.2 \text{ cm}^{-1}$ and $x_{11} = -0.02 \pm 0.02 \text{ cm}^{-1}$. Two other bands not attributable to the solvent were observed: one could be assigned to $\nu_3(t_2)$ but the other, at 111.3 cm^{-1} , could not be attributed to SnI_4 . This band was not observed in the Raman spectrum recorded with 514.5-nm excitation and is possibly due to a photolysis

Table VI. Wavenumbers and Assignments of the Bands in the Resonance Raman Spectrum of Tin Tetraiodide in Cyclohexane Solution

assignt	$\tilde{\nu}/\text{cm}^{-1}$ ^a	$\tilde{\nu}/\text{cm}^{-1}$ ^b	assignt	$\tilde{\nu}/\text{cm}^{-1}$ ^a	$\tilde{\nu}/\text{cm}^{-1}$ ^b
$\nu_2(e)$		43	$7\nu_1(A_1)$	1056.9 ± 0.5	1053.5
$\nu_4(t_2)$		63	$8\nu_1(A_1)$	1207.8 ± 0.5	1204.5
?	111.3 ± 0.8		$9\nu_1(A_1)$	1358.7 ± 1	1355.5
$\nu_1(a_1)$	150.5 ± 0.5	151	$10\nu_1(A_1)$	1508 ± 3	1506
$\nu_3(t_2)$	219.4 ± 1.0	221	$11\nu_1(A_1)$	1658 ± 5	1653
$2\nu_1(A_1)$	302.5 ± 0.5	302	$12\nu_1(A_1)$	1812 ± 5	
$3\nu_1(A_1)$	453.1 ± 1.0	453	$13\nu_1(A_1)$	1972 ± 5	
$4\nu_1(A_1)$	605.8 ± 0.5	602	$14\nu_1(A_1)$	2110 ± 5	
$5\nu_1(A_1)$	756.5 ± 0.5	759.5	$15\nu_1(A_1)$	2255 ± 5	
$6\nu_1(A_1)$	907.8 ± 0.5	903.5			

^a Present work. ^b References 1 and 3.

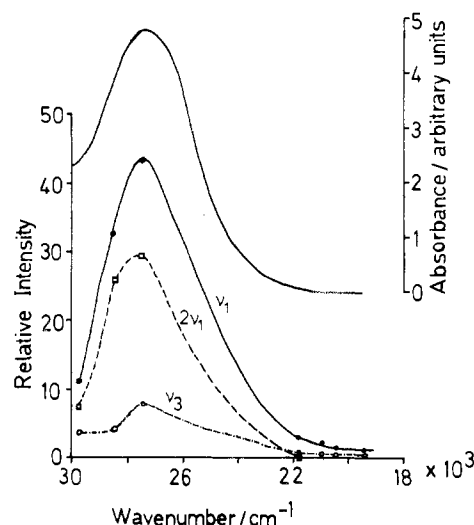


Figure 5. Excitation profiles for ν_1 , $2\nu_1$, and ν_3 and the absorption spectrum of SnI_4 in cyclohexane solution.

product formed during UV irradiation.

It was possible to obtain reliable intensity data with UV exciting lines, and excitation profiles were constructed for ν_1 , $2\nu_1$, and ν_3 by using the 802-cm^{-1} band of cyclohexane as an internal intensity standard. These are presented in Figure 5, together with the absorption spectrum of SnI_4 in cyclohexane solution. Examination of these excitation profiles reveals an A -term resonance enhancement for ν_1 and $2\nu_1$, the intensity maximizing in the region of the absorption maximum, i.e., the Franck-Condon maximum. The excitation profile for ν_3 also peaks in the same region but the enhancement is less than that for ν_1 . The Raman intensity of ν_1 observed with 363.8 nm is 44 times that with 514.5-nm excitation, whereas the corresponding factor for ν_3 is 32. The intensity enhancement of ν_3 is most likely to be due to A -term scattering resulting from Jahn-Teller coupling in the degenerate excited state since we would expect B -term enhancement to be much the smaller (especially because the the first- and second-lowest excited states are separated by as much as 7500 cm^{-1}). As with SiI_4 , the smaller enhancement of ν_3 relative to ν_1 , may be interpreted as a smaller shift of the excited-state potential curve along Q_3 than along Q_1 .

Comparison with Resonance Raman Studies of Other Tetrahalide Species. Details of the resonance Raman spectra of GeI_4 and SnI_4 are collated in Table VII, together with those of other tetrahalide species reported in the literature. An examination of these data shows that the anharmonicity constant x_{11} is small and negative and that in most cases a long overtone progression in ν_1 is observed. It occurred to us that these two observations may be correlated. It can be seen that,

(11) F. Hoefler, W. Sawodny, and E. Hengge, *Spectrochim. Acta, Part A*, **26A**, 819 (1970).

(12) R. J. H. Clark and B. Stewart *Struct. Bonding (Berlin)*, **36**, 1 (1979).

Table VII. Resonance Raman Spectroscopic Data on Some Tetrahalide Species

species	state	assign ^a	λ_{\max}/nm	λ_0/nm	ω_1/cm^{-1}	x_{11}/cm^{-1}	progression	$I(2\nu_1)/I(\nu_1)$	ref
GeI ₄	cyclohexane soln	¹ T ₂ ← ¹ A ₁	360.4	363.8	158.9 ± 0.1	-0.09 ± 0.02	7ν ₁	0.68	b
SnI ₄	cyclohexane soln	¹ T ₂ ← ¹ A ₁	364.5	363.8	151.2 ± 0.2	-0.02 ± 0.02	15ν ₁	0.85	b
TiBr ₄	cyclohexane soln	¹ T ₂ ← ¹ A ₁	348.7	363.8	232.9 ± 0.1	-0.07 ± 0.01	11ν ₁	0.68	c
TiI ₄	cyclohexane soln	¹ T ₂ ← ¹ A ₁	515.5	514.5	161.5 ± 0.2	-0.11 ± 0.03	13ν ₁	0.61	d
[Et ₄ N] ⁺ [FeCl ₄] ⁻	nitromethane soln	⁶ T ₂ ← ⁶ A ₁	364.0	363.8	335.4	-0.6	4ν ₁	0.28	e
[Et ₄ N] ⁺ [FeBr ₄] ⁻	nitromethane soln	⁶ T ₂ ← ⁶ A ₁	472.0	476.5	202.0 ± 0.2	-0.38 ± 0.05	7ν ₁	0.45	f
[Et ₄ N] ⁺ [FeI ₄] ⁻	CsI disk, 100 K	⁶ T ₂ ← ⁶ A ₁	699.0	647.1	141.3 ± 0.3	-0.3 ± 0.1	3ν ₁	0.38	g

^a The assignment relates to that of the resonant electronic transition. ^b Present work. ^c R. J. H. Clark and T. J. Dines, *Chem. Phys. Lett.*, 64, 499 (1979). ^d R. J. H. Clark and P. D. Mitchell, *J. Am. Chem. Soc.*, 95, 8300 (1973); *J. Raman Spectrosc.*, 2, 399 (1974). ^e R. J. H. Clark and T. J. Dines, to be submitted for publication. ^f R. J. H. Clark and P. C. Turtle, *J. Chem. Soc., Faraday Trans. 2*, 72, 1885 (1976). ^g R. J. H. Clark and P. C. Turtle, unpublished work.

as a general rule, the smaller the magnitude of x_{11} , the greater is the number of overtones observed, taking account of the wavenumber difference between the exciting line and the resonant electronic transition. The extent of an overtone progression is controlled by one or more of four factors: (1) the closeness to resonance, which determines the magnitudes of the denominators in eq 3; (2) the extent to which the equilibrium configuration is distorted along the normal coordinate Q in the excited state, which determines the relative magnitudes of the Franck-Condon factors $\langle f|v\rangle\langle v|i\rangle$; (3) the relaxation time for each overtone possibly being different. [The fwhm of a Raman band is inversely proportional to the vibrational relaxation time; hence the increase in fwhm for successive overtones (which eventually becomes so large that overtones can no longer be distinguished from the background count) may reflect a progressive decrease of the relaxation time.]; (4) the increase of the fwhm for successive overtones may be due to the presence of overlapping hot bands since ν_1 is, in reality, a superposition of several hot bands of the type $(\nu_1\nu_1 + \nu_i) - \nu_i$, where ν_i is a low-lying fundamental.

We believe that this last factor may be of great significance for the tetraiodides, which have two low-lying degenerate deformation modes $\nu_2(e)$ and $\nu_4(t_2)$. Figure 6 shows the relative populations of the levels of ν_1 , ν_2 , ν_3 , and ν_4 of SnI₄ at 298.15 K. For the degenerate deformation modes ν_2 and ν_4 , the population sums are substantial and a simple calculation shows that the fraction of molecules in the ground vibrational state is less than 10^{-4} . Therefore, for SnI₄ each overtone of ν_1 will be the superposition of a large number of hot bands of the type $(\nu_1\nu_1 + \nu_2\nu_2) - \nu_2\nu_2$ and $(\nu_1\nu_1 + \nu_4\nu_4) - \nu_4\nu_4$. The wavenumber of each of these hot bands will depend on the value of x_{11} and on the cross-terms x_{12} and x_{14} in the potential function. However, the increase in the "spread" of the hot-band positions for successive overtones will be principally controlled by x_{12} and x_{14} . When a subsidiary progression $\nu_1\nu_1 + \nu_i$ is observed an approximate value for x_{1i} can be obtained but no such progressions were observed for SnI₄. If the presence of hot bands is a more important factor than vibrational relaxation in determining the fwhm of an overtone, we may conclude that for SnI₄, and to a lesser extent GeI₄, the cross-terms x_{12} and x_{14} are very small.

Conclusions

The following general conclusions have been drawn from the resonance Raman spectroscopic data obtained for the group 4 tetraiodides:

1. There is a strong resonance enhancement of the band attributable to the totally symmetric stretching fundamental $\nu_1(a_1)$, due to *A*-term scattering arising from the lowest dipole-allowed transition which, under rigorous resonance conditions, gives rise to a long overtone progression. This indicates that there is a significant displacement along the normal coordinate Q_1 in the resonant electronic transition.

2. There is some evidence for Jahn-Teller distortion in the excited state, especially for SiI₄ and SnI₄ (for which we have

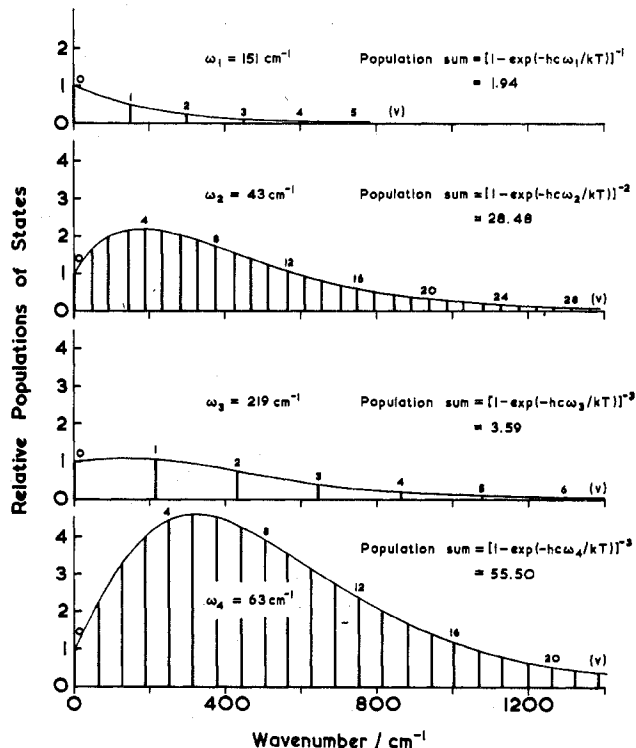


Figure 6. Populations of vibrational states of SnI₄ at 298.15 K relative to the ground-state population (set = 1.0 for each fundamental). $Q_{\text{vib}}^{\text{harm}} = 10998$.

intensity data), along the normal coordinate Q_3 . Since the intensity enhancement of $\nu_3(t_2)$ is smaller than that of $\nu_1(a_1)$ and there are no overtone or combination tone progressions involving ν_3 , we may infer that the Jahn-Teller effect is small. We might therefore expect the geometry in the excited state to be slightly distorted from tetrahedral, the probable symmetry being C_{3v} in view of the nature of the Jahn-Teller-active mode.

3. There is only a very small enhancement of the bands attributable to the deformation modes $\nu_2(e)$ and $\nu_4(t_2)$.

There is a complication in the interpretation of the intensity data not considered above, in that both *A*-term (Jahn-Teller) and *B*-term (Herzberg-Teller) scattering are allowed for the nontotally symmetric modes of a tetrahedral molecule. It is therefore possible for interference to occur between *A*- and *B*-term contributions to the transition polarizability. Such an effect has been observed by Shelnutz et al.¹³ in the resonance Raman spectra of some metalloporphyrins. The effect manifests itself in a distortion of the excitation profile. However, in the present study we were unable to measure excitation

(13) J. A. Shelnutz, L. D. Cheung, R. C. C. Chang, Y. Nai-Teng, and R. H. Felton, *J. Chem. Phys.*, 66, 3387 (1977).

profiles in sufficient detail due to the lack of suitable UV laser lines. We cannot therefore assess quantitatively the importance of *B*-term scattering for the nontotally symmetric modes of these tetraiodide species, although we might reasonably expect it to be small in view of the large separation of the first two excited states.

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Contribution from the Department of Chemistry,
Florida State University, Tallahassee, Florida 32306

Nuclear Magnetic Resonance Studies of Lanthanide Dicarboxylate Complexes in Solution

GREGORY R. CHOPPIN* and LENNART KULLBERG

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¹H NMR and ¹³C shift data were measured for complexes of La(III), Pr(III), Eu(III), and Yb(III) with ethylene-1,2-dioxydiacetate (EDODA), ethylene-1,2-dithiodiacetate (EDSDA), and ethylene-1,2-diaminodiacetate (EDDA). In the EDSDA complexes, the data indicate that the sulfur atoms do not participate in bonding to the lanthanide cations. Both carboxylate groups bind to Pr and Eu, but only a single carboxylate group interacts with Yb. The EDDA and EDODA complexes are tetradentate with long-lived Ln-N bonds in LnEDDA but short-lived Ln-O(ether) bonds in LnEDODA.

Introduction

A thermodynamic study of the complexation of lanthanide cations by ethylene-1,2-dioxydiacetate (EDODA) and the analogous ethylene-1,2-dithiodiacetate (EDSDA) and ethylene-1,2-diaminodiacetate (EDDA) has been reported by Grenthe and Gardhammar.¹ Similar studies were reported from this laboratory for complexing by benzene-1,2-dioxydiacetate (BDODA).² The data for BDODA, EDODA, and EDDA were interpreted as reflecting tetradentation by the ligand involving the amino and the ether oxygen donors. However, the thio ligand EDSDA formed weaker complexes which indicated a probable lack of involvement of the thio donors in bonding to the lanthanide cations.

The tetradentation of the BDODA complexes was confirmed by a study of the ¹H and ¹³C nuclear magnetic resonance spectra of the ligand when complexed by the paramagnetic ions Pr(III), Eu(III), and Yb(III).³ From analysis of the induced shifts, internuclear distances and angles in the complex could be calculated. The ML complex had a planar chelate ring with metal-oxygen distances of 2.2 ± 0.1 Å for both ether oxygen and carboxylate oxygen donors.

In this paper we report on a study of the ¹H and ¹³C NMR spectra of the complexes of EDODA, EDDA, and EDSDA with the same three paramagnetic lanthanides (i.e., Pr, Eu, and Yb). The purpose of the study was to obtain information on the structure of the complexes in solution with particular regard to the question of the participation of the ether oxygen, the nitrogen, and the sulfur atoms in the coordination of the ligands to the metals. Our earlier study of BDODA complexes had shown that the three paramagnetic ions, Pr(III), Eu(III), and Yb(III), were a satisfactory set for obtaining insight into such structural details of complexes in solution.

If we assume axial symmetry, the lanthanide-induced dipolar shift ($\Delta\delta$) can be described by the McConnell-Robertson equation^{4,5} (1), where *r* is the distance between the metal and

$$\Delta\delta = C(3 \cos^2 \theta - 1)/r^3 \quad (1)$$

the nucleus being observed, θ is the angle which the principal magnetic axis makes with a line drawn from the metal to the nucleus, and *C* is a proportionality constant for a given complex. Obviously, the cos² function leads to a zero shift for $\theta = 54^\circ 44'$.

A major question in the application of the LIS theory involving eq 1 to calculations of ligand structure involves the requirement of axial symmetry. The details of structure are known for relatively few lanthanide complexes in solution. However, invariance in shift ratios with several lanthanide ions is used as a satisfactory test for axial symmetry.^{6,7} Horrocks⁸ has discussed the question of the apparent presence of "effective" axial symmetry in solution complexes while Pennington and Cavanaugh have demonstrated the use of the LIS theory even for such flexible, dynamic complexes as those formed by benzoic acids.⁹

In order to use the shifts in the McConnell-Robertson equation, it is necessary also to ascertain that the experimental shifts are purely dipolar or to correct for any contact contribution. This can be achieved usually by using more than one paramagnetic lanthanide ion since the relative contribution of the two mechanisms^{10,11} to the observed shift is different for different cations. However, if the lanthanide ions form complexes with the same structure and the shifts are purely dipolar, the shift ratio should be constant irrespective of the particular nucleus measured. In isostructural complexes of Pr(III), Eu(III), and Yb(III), the Pr(III)-induced dipolar shift is of opposite sign from that of the shifts of Eu(III) and Yb(III). In such complexes, the absolute magnitude of the dipolar shifts decreases in the sequence Yb(III) > Pr(III) > Eu(III).

- (4) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).
- (5) R. M. Golding and P. Pyykko, *Mol. Phys.*, **26**, 1399 (1973).
- (6) B. Bleaney, C. M. Dobson, B. A. Levine, R. M. Martin, R. J. P. Williams, and A. Xavier, *J. Chem. Soc., Chem. Commun.*, 791, (1972).
- (7) T. D. Marinetti, G. H. Snyder, and B. D. Sykes, *Biochemistry*, **15**, 4600 (1976).
- (8) W. DeW. Horrocks, *J. Am. Chem. Soc.*, **96**, 3022 (1974).
- (9) B. T. Pennington and J. R. Cavanaugh, *J. Magn. Reson.*, **31**, 11 (1978).
- (10) J. F. Desreux and C. N. Reilley, *J. Am. Chem. Soc.*, **98**, 2105 (1976).
- (11) C. N. Reilley, B. W. Good, and R. D. Allendoerfer, *Anal. Chem.*, **48**, 1446 (1976).

- (1) I. Grenthe and G. Gardhammar, *Acta Chem. Scand., Ser. A*, **28**, 125 (1974).
- (2) Y. Hasegawa and G. R. Choppin, *Inorg. Chem.*, **16**, 2931 (1977).
- (3) L. Kullberg and G. R. Choppin, *Inorg. Chem.*, **16**, 2926 (1977).