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Published in:
Journal of Chemical Physics

Link to article, DOI:
[10.1063/1.441451](https://doi.org/10.1063/1.441451)

Publication date:
1981

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Adams, D. M., Berg, R. W., & Williams, A. D. (1981). Vibrational spectroscopy at very high pressures. Part 28. Raman and far-infrared spectra of some complex chlorides A_2MCl_6 under hydrostatic pressure. *Journal of Chemical Physics*, 74(5), 2800-2807. <https://doi.org/10.1063/1.441451>

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Vibrational spectroscopy at very high pressures. Part 28. Raman and far-infrared spectra of some complex chlorides A_2MCl_6 under hydrostatic pressure^{a)}

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(Received 10 November 1980; accepted 18 November 1980)

Raman and far-IR mode frequency shifts with pressure have been observed under hydrostatic conditions in a gasketed diamond anvil cell (d.a.c.). Using compressibilities calculated from unit cell constants and lattice energies, Grüneisen parameters γ , have been obtained for all observed modes. Where previous data exist for comparison, it is shown that use of a d.a.c. without gaskets (i.e., applying a shear stress to the sample) greatly underestimates the true shifts of IR modes in particular. The Grüneisen parameter γ_1 for $a_{1g} \bar{\nu}_1$ of the complex ions is always greater than γ_2 . It is shown that this is due to the greater value of anharmonicity of $\bar{\nu}_1$, as is the increase in γ_1 , γ_2 , and γ_3 in the series A_2MCl_6 , where $A = Cs, Rb, K$. Grüneisen parameters for K_2SnCl_6 and Rb_2TeCl_6 are greater than for non-transition metal complexes. Anomalies in the $\bar{\nu}_i$ versus pressure curves for K_2SnCl_6 and $[(CH_3)_6N]_2MCl_6$ ($M = Sn, Te, Pt$) are discussed in relation to their structures. Shifts of $\bar{\nu}_i$ with temperature for K_2ReCl_6 and K_2PtCl_6 are analyzed into explicit and implicit anharmonic contributions.

I. INTRODUCTION

When a hydrostatic pressure is applied to a solid there is a shift of the phonon frequencies due to the existence of anharmonic terms in the potential function. In seeking to understand these shifts in terms of structural and geometrical changes induced by an applied stress there are, broadly, two lines of approach. Firstly, we may analyze our data in terms of lattice dynamical theories. Secondly, we may attempt to identify operative factors in a qualitative way by study of series of structurally related materials. Properly handled, these two approaches converge, but we believe that the latter is of particular value in giving a qualitative understanding before detailed calculations are attempted.

In this context hexahalide complexes A_2MX_6 are particularly attractive due to the large number of them and the parameters which may be varied. We report a study of the far-IR and Raman spectra under high pressures, of the compounds shown in the tables. These spectra were obtained using a diamond anvil cell (d. a. c.) with a metal gasket between the anvils. The sample is contained within a gasket hole ~ 0.4 mm diameter and of depth up to 0.25 mm: Inside the hole a fluid is placed (commonly 4:1 methanol: ethanol mixture) which is used to transmit the pressure to the solid sample suspended within it. The pressure on the solid is therefore hydrostatic to a good approximation, at least within the pressure range (up to 50 kbars) ($1 \text{ kbar} = 10^8 \text{ N m}^{-2}$) which we have used. In contrast, use of a d. a. c. without a gasket results in a severely nonhydrostatic pres-

sure being applied to the solid sample trapped between the diamond anvils. This is somewhat less objectionable for Raman than for IR work, as the laser beam can be focused on a very small spot of sample which, to a poor approximation, can be regarded as under a hydrostatic pressure. In the far-IR region, wavelengths are being used which approach the aperture of the d. a. c. and the whole sample, with its pressure gradients, therefore contributes to the spectrum.

We have reported previously on the IR and Raman spectra of various A_2MX_6 complexes under nonhydrostatic pressures in a d. a. c. used without a gasket.¹⁻⁴ In order to provide accurate data suitable for theoretical analysis we have repeated and extended many of these measurements under hydrostatic conditions. In general, we have been unable to obtain high pressure far-IR spectra below 100 cm^{-1} as diffraction at the gasket edges then becomes severe. Accordingly we have few data on the IR-active lattice mode behavior under hydrostatic pressure. However, its qualitative behavior relative to internal modes $\bar{\nu}_3$ and $\bar{\nu}_4$ (also of T_{1u} symmetry) of octahedral MX_6^{2-} is known from earlier work.

II. EXPERIMENTAL

The d. a. c., Raman and far-IR instruments, and optical layout used have been described elsewhere^{4,5} as has the ruby R -line pressure calibration technique.^{6,7} For far-IR spectroscopy, samples were placed in 0.4 mm diameter holes in inconel or molybdenum gaskets initially 0.050 or 0.075 mm thick with Nujol as the pressure-transmitting fluid. Nujol freezes ~ 13 kbars but is compatible with far-IR spectroscopy whereas methanol:

^{a)}Part 27 is D. M. Adams, and S. K. Sharma, *J. Mol. Struct. Solids* (accepted for publication).

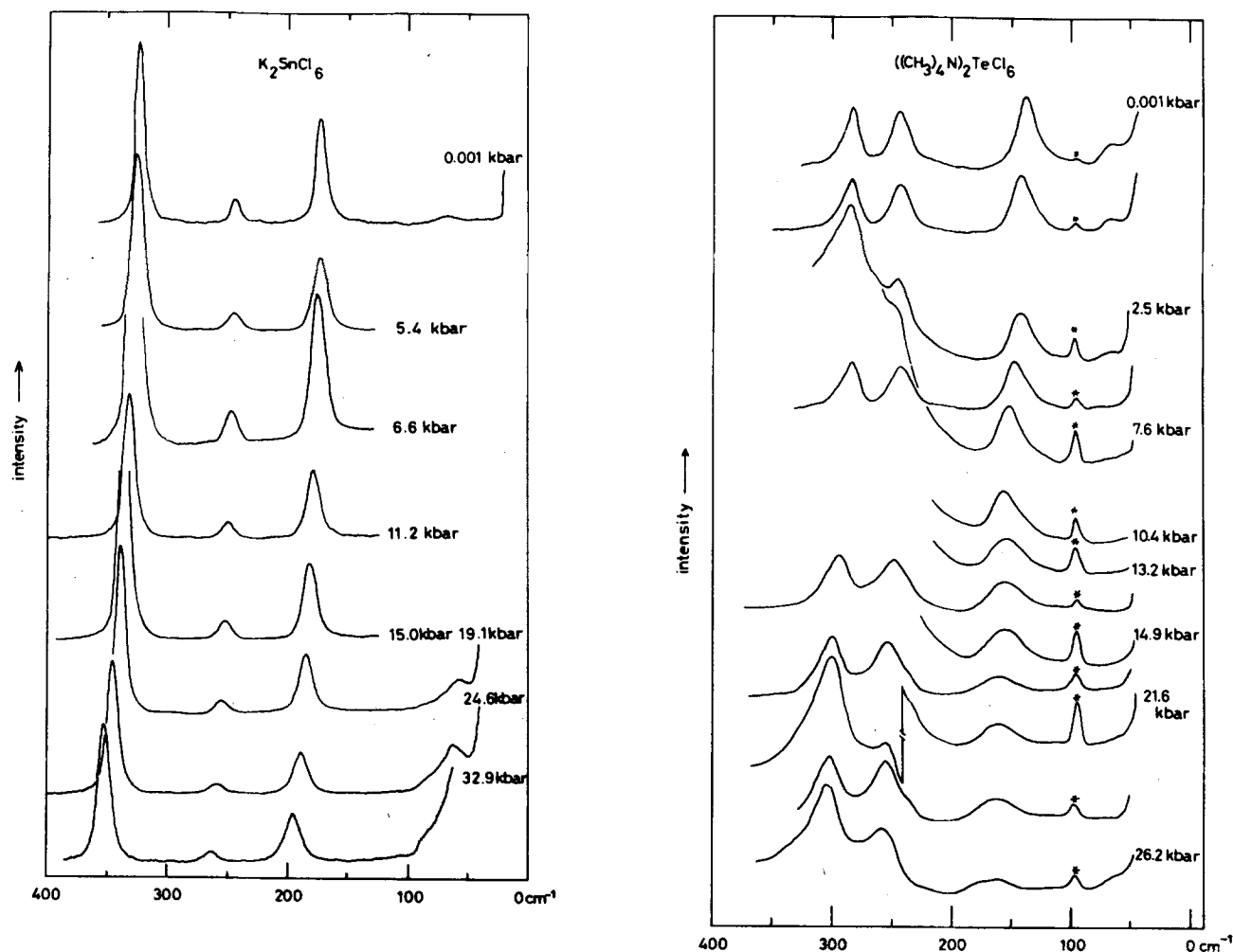
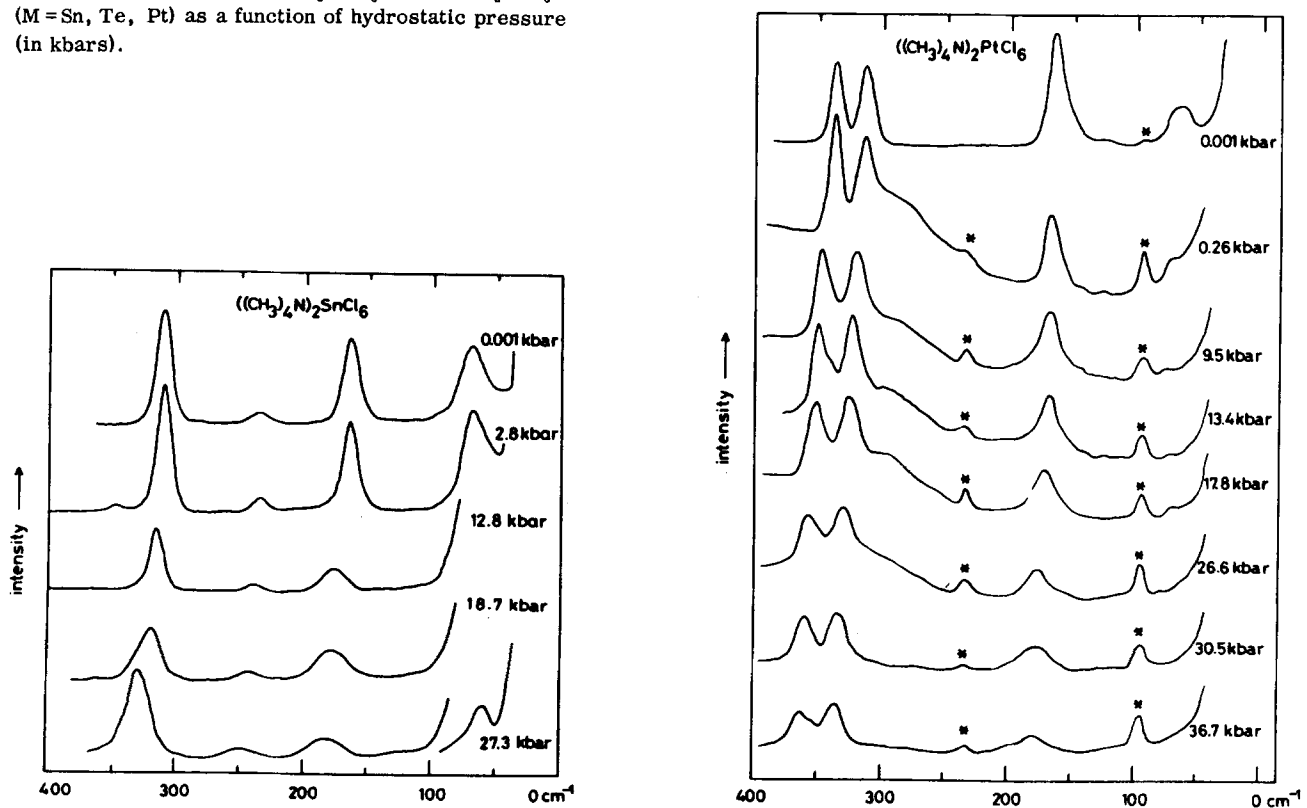


FIG. 1. Raman spectra of K_2SnCl_6 and $(TMA)_2MCl_6$ ($M = Sn, Te, Pt$) as a function of hydrostatic pressure (in kbars).



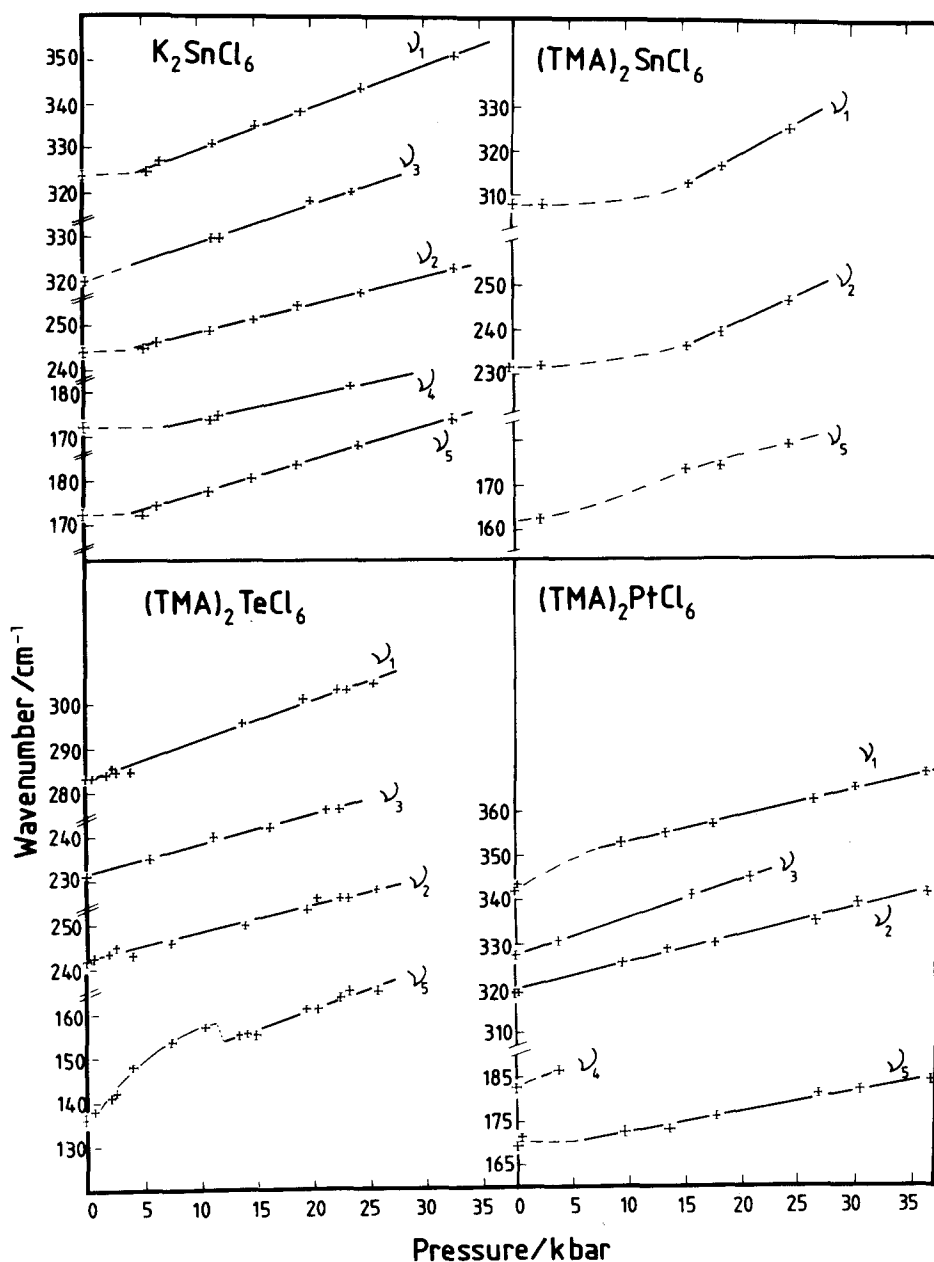


FIG. 2. Plots of $\bar{\nu}_i$ versus pressure at room temperature.

ethanol is not. Raman work was done with similar gas-gaskets but of an initial thickness of 0.25 mm; the pressure-transmitting fluid was either 4:1 methanol: ethanol or Nujol. The Raman spectra were at about 4 or 5 cm^{-1} resolution.

III. RESULTS

Examples of the spectra obtained as a function of pressure are shown in Fig. 1. When the band wavenumbers were plotted against pressure (P in kbars), good straight lines were obtained for the compounds having monatomic cations, except that for K_2SnCl_6 the mode wavenumbers are apparently characterized by an initial pressure insensitivity [Fig. 2(a)]. In contrast, the tetramethylammonium (TMA) salts showed nonlinear behavior [Figs. 2(b)–2(d)]. The temperature dependence is shown in Fig. 3.

These data were analyzed by least squares regression with the results shown in Table I. The number of points (n) used for estimation of the slopes $\Delta\bar{\nu}_i/\Delta P$ are given, as well as the standard statistical coefficient of determination r^2 which approaches unity for a perfect linear relationship between pressure (x) and wave number (y).

IV. THEORETICAL CONSIDERATIONS

If a crystal having only harmonic forces were compressed, the equilibrium positions of the atoms would be closer together but the force constants would remain the same as in the absence of applied pressure. Hence, in the harmonic approximations, a mode $\bar{\nu}_i$ has no pressure (or temperature) dependence. Anharmonic terms (cubic and quartic) must be added to the potential energy function U to account for these and other manifestations of the interaction of normal modes. Thus Eq. (1)

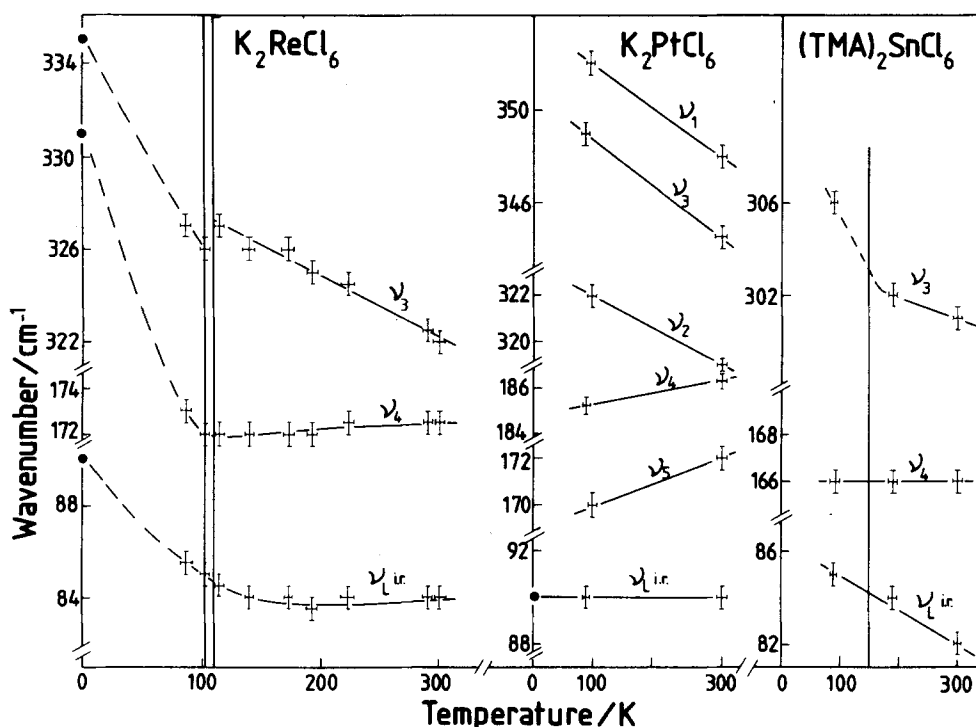


FIG. 3. Temperature dependence of $\tilde{\nu}_i$ at ambient pressure. Known phase transitions at 103, 111 (Re), and 148 K (Sn) are indicated by vertical lines. \circ = data of O'Leary and Wheeler³⁶ or Dorain and Wheeler.³⁷

$$U = U_0 + \frac{1}{2} \sum_{\alpha\beta} k_{\alpha\beta}(ll') u_\alpha(l) u_\beta(l') + \frac{1}{6} \sum_{\alpha\beta\gamma} k_{\alpha\beta\gamma}(ll'l'') u_\alpha(l) u_\beta(l') u_\gamma(l'') + \dots, \quad (1)$$

where U_0 is the minimum value of the potential energy,

$$k_{\alpha\beta}(ll') = \left[\frac{\partial^2 U}{\partial u_\alpha(l) \partial u_\beta(l')} \right]_0,$$

and

$$k_{\alpha\beta\gamma}(ll'l'') = \left[\frac{\partial^3 U}{\partial u_\alpha(l) \partial u_\beta(l') \partial u_\gamma(l'')} \right]_0.$$

The α -Cartesian component of the displacement of the l th atom from its equilibrium position is given by $u_\alpha(l)$.

Phenomenologically, the volume dependence of a crystal normal mode $\tilde{\nu}_i(\mathbf{k})$ of wave vector \mathbf{k} is represented by the mode Grüneisen parameter $\gamma_i(\mathbf{k})$, which is the constant relating the fractional increase of a crystal frequency caused by a pressure-induced fractional volume decrease $-\Delta V/V$, Eq. (2).

$$\frac{\Delta \tilde{\nu}_i(\mathbf{k})}{\tilde{\nu}_i(\mathbf{k})} = \gamma_i(\mathbf{k}) \left(-\frac{\Delta V}{V} \right). \quad (2)$$

For convenience we omit \mathbf{k} from $\gamma_i(\mathbf{k})$ and $\tilde{\nu}_i(\mathbf{k})$ in the following discussion. γ_i may be related as shown by Eq. (3) to experimentally accessible quantities:

$$\gamma_i = - \left(\frac{d \ln \tilde{\nu}_i}{d \ln V} \right)_T = \frac{1}{\chi_T} \left(\frac{d \ln \tilde{\nu}_i}{d P} \right)_T = \frac{1}{\chi_T \tilde{\nu}_i} \left(\frac{d \tilde{\nu}_i}{d P} \right)_T, \quad (3)$$

where $\chi_T = -(1/V)(\partial V/\partial P)$ is the isothermal volume compressibility. Values of the relative shift $(1/\tilde{\nu}_i) \times (d\tilde{\nu}_i/dP)_T$ are shown in Table II in per cent per kbar.

Since the relative shift differs from γ_i only by a constant (χ_T), relative shifts may be compared directly for any one material.

However, in order that mode shifts may be compared accurately between different compounds, values of their compressibilities χ_T are needed. These data have not been reported for our compounds, except for K_2ReCl_6 ,⁸ but estimates can be made using an atomistic relationship in a form due to Plendl, Mitra, and Gielisse.⁹ Thus,

$$\chi_T = \frac{mZN}{\eta} \left(\frac{V}{E} \right) = \frac{mZN}{\eta} \left(\frac{a_0^3}{E} \right), \quad (4)$$

where η = number of atoms per cubic unit cell of volume V and side a_0 , m = number of component atoms, N = Avogadro's constant, Z = maximum valency of an ion or complex ion, and E = lattice energy. Since m , η , and Z are constants for our series (excluding TMA salts), the compressibilities scale as a_0^3/E .

Using literature values¹⁰ for a_0 and E , the compressibilities shown in Table III were calculated. It is gratifying that the calculated compressibility for K_2ReCl_6 is of the same order of magnitude as the reported experimental value at 300 K.

The mode Grüneisen parameters γ_i Table IV, calculated using the data of Tables II and III, may now be compared throughout the series of materials used.

Although the Grüneisen parameter is useful in describing the consequences of anharmonic mode interactions, there is no explicit recognition of anharmonicity in Eq. (3). General expressions for pressure-induced mode shifts have been deduced by Maradudin, beginning from an anharmonic potential function.¹¹ These are of great complexity but are capable of simpli-

TABLE I. Vibrational frequencies (cm^{-1}) and their shifts with pressure for complex halides A_2MY_6 .

	$\tilde{\nu}_1$				$\tilde{\nu}_2$				$\tilde{\nu}_3$			
	$\tilde{\nu}_0^a$	$\Delta\tilde{\nu}/\Delta P^b$	n^c	r^2^d	$\tilde{\nu}_0$	$\Delta\tilde{\nu}/\Delta P$	n	r^2	$\tilde{\nu}_0$	$\Delta\tilde{\nu}/\Delta P$	n	r^2
K_2PdCl_6									357	0.70	6	0.99
K_2ReCl_6	357.5	0.90	10	0.995					330 ^e	0.61	12	0.91
K_2OsCl_6									321 ^e	0.83	4	0.99
K_2IrCl_6									336	0.51	4	0.99
K_2PtCl_6	351	0.78	12	0.994	321	0.49	12	0.989	345	0.81	10	0.95
Rb_2PtCl_6	345.5	0.68	6	0.989	318	0.43	6	0.985	342	0.48 ^f	6	0.99
Cs_2PtCl_6	335.3	0.59	3	0.99	311	0.31	3	0.979	332	0.52	6	0.996
Tl_2PtCl_6									335	0.45	5	0.97
$(TMA)_2PtCl_6^g$	339.5	0.69	8	0.98	315	0.61	8	0.99	328	0.82	4	0.998
K_2PtBr_6	218.5	0.48	8	0.91	195.5	0.29	8	0.97	244.5	0.42	6	0.99
K_2SnCl_6	320.7 ^e	0.96	7	0.997	242 ^e	0.67	7	0.998	320	0.89	5	0.995
$(TMA)_2SnCl_6$	308	0.64	5	0.96	232	0.56	5	0.97				
Rb_2TeCl_6	300	1.09	8	0.998	253	0.64	8	0.998	~252	0.82	7	0.98
$(TMA)_2TeCl_6$	282	0.8 ^f	3	0.81	241	1.0 ^f	4	0.86	~232	0.67	6	0.99

	$\tilde{\nu}_4$				$\tilde{\nu}_5$				$\tilde{\nu}_L$ (IR)			
	$\tilde{\nu}_0$	$\Delta\tilde{\nu}/\Delta P$	n	r^2	$\tilde{\nu}_0$	$\Delta\tilde{\nu}/\Delta P$	n	r^2	$\tilde{\nu}_0$	$\Delta\tilde{\nu}/\Delta P$	n	r^2
K_2PdCl_6												
K_2ReCl_6	180 ^e	0.29	11	0.96	176	0.79	10	0.99	90	0.43	8	0.99
K_2OsCl_6	178	0.30	4	0.96								
K_2IrCl_6	184	0.41	4	0.92								
K_2PtCl_6	184	0.62	10	0.98	174	0.66	12	0.999	91	0.66	11	0.97
Rb_2PtCl_6	187	0.48	5	0.99	174	0.79	6	0.998				
Cs_2PtCl_6	186	0.66	6	0.995	172	1.05	4	0.909				
Tl_2PtCl_6	181	0.28	5	0.97								
$(TMA)_2PtCl_6^g$	182.5	1.0 ^f	2	1.00	165	0.39	8	0.995				
K_2PtBr_6					114.5	0.74	8	0.98	80 ^f	0.30	8	0.99
K_2SnCl_6	172	0.43	4	0.90	169 ^e	0.80	7	0.999				
$(TMA)_2SnCl_6$					164	0.71	5	0.96				
Rb_2TeCl_6	125 ^h	0.65	4	0.70	142	0.91	8	0.997	52 ^f	0.79	4	0.996
$(TMA)_2TeCl_6$					136	2.2 ^f	5	0.996				

^aValue at ambient pressure.^bIn $\text{cm}^{-1} \text{kbar}^{-1}$.^cNo. of points.^dCoefficient of determination: $r^2 = [\sum(x - \bar{x})(y - \bar{y})]^2 / [\sum(x - \bar{x})^2 \sum(y - \bar{y})^2]$, $\bar{x} = (\sum x/n)$.^eTMA = tetramethylammonium.^fRaman-active lattice mode.^gRegression value; for experimental values see Fig. 1 or references.^hAbsent at ambient pressure; appears at elevated pressure.ⁱInitial slope.TABLE II. Relative shifts $1/\tilde{\nu}_i(k) [d\tilde{\nu}_i(k)/dP]_T$ for complex halides A_2MX_6 under hydrostatic pressure (10^{-2}kbar^{-1}).

	$\tilde{\nu}_1$	$\tilde{\nu}_2$	$\tilde{\nu}_3$	$\tilde{\nu}_4$	$\tilde{\nu}_5$	$\tilde{\nu}_L$ (IR)	$\tilde{\nu}_L$ (Ra.)
K_2PdCl_6	a	...	0.20
K_2ReCl_6	0.25	b	0.18	0.16	0.45	0.48 ^c	...
K_2OsCl_6	a	...	0.26	0.17
K_2IrCl_6	a	...	0.15	0.22
K_2PtCl_6	0.22	0.15	0.23	0.34	0.38	0.73	...
Rb_2PtCl_6	0.20	0.14	0.14	0.26	0.45
Cs_2PtCl_6	0.18	0.10	0.16	0.35	0.61
Tl_2PtCl_6	0.13	0.15
$(TMA)_2PtCl_6^d$	0.20	0.19	0.25	0.55	0.24
K_2PtBr_6	0.22	0.15	0.17	...	0.65	...	0.38
K_2SnCl_6	0.30	0.28	0.28	0.25	0.47
$(TMA)_2SnCl_6$	0.21	0.24	0.45
Rb_2TeCl_6	0.36	0.25	0.33	0.52	0.64	...	1.52
$(TMA)_2TeCl_6$	0.28	0.41	0.29	...	1.62

^aRaman spectra could not be obtained for these deeply colored materials.^b $\tilde{\nu}_2$ is vanishingly weak.^cApproximate value.^dTMA = tetramethylammonium.

TABLE III. Compressibilities for complex halides A₂MX₆ calculated using Eq. (4) [$m=3$, $Z=2$, $\eta=36$. $\chi_T=1.0037 \times 10^{-5}$ (α_0^3/E) bar⁻¹].^a

	a_0 (Å)	E (kJ mol ⁻¹)	$\chi_T/(10^{-6}$ bar ⁻¹)	
			Calc.	Expt.
K ₂ PdCl ₆	9.75	1481 ^b	6.28	
K ₂ ReCl ₆	9.84	1416 ^c	6.75	7.2 ^d
K ₂ OsCl ₆	9.729	1447	6.39	
K ₂ PtCl ₆	9.755	1468 ^c	6.35	
Rb ₂ PtCl ₆	9.901	1464	6.65	
Cs ₂ PtCl ₆	10.215	1444	7.41	
Tl ₂ PtCl ₆	9.779	1546	6.01	
K ₂ PtBr ₆	10.293	1423 ^c	7.69	
K ₂ SnCl ₆	10.002	1352 ^c	7.43	
Rb ₂ TeCl ₆	10.233	1321 ^e	8.14	

^aData from Ref. 10 unless otherwise stated.^bFor (NH₄)₂PdCl₆.^cSimilar values are quoted in Ref. 33.^dReference 8.^eA value of 334 ± 17 kcal mol⁻¹ (≡ 1398 ± 71 kJ mol⁻¹) is given in Ref. 34.

fication for some special cases. For a uniform external pressure P applied to a face-centered cubic crystal described by the nearest neighbor central force field, we have Eq. (5), where r_0 is the nearest neighbor interatomic distance, $k_{\alpha\beta}$ the harmonic, and $k_{\alpha\beta\gamma}$ the cubic anharmonic force constant:

$$\frac{1}{\bar{\nu}_i} \left(\frac{d\bar{\nu}_i}{dP} \right)_T \propto \frac{r_0^2 k_{\alpha\beta\gamma}}{k_{\alpha\beta}^2} \quad (5)$$

The inverse dependence upon the quadratic force constant accords with experience, and the direct proportionality of the stress-induced relative shift to cubic anharmonicity emphasizes the fact that its existence is a consequence of the failure of the harmonic approximation. Since the materials we have studied are of the antiferroite lattice type, the approximations underlying Eq. (5) are not unreasonable, and the equation is therefore taken as a tolerable first-order description of the behavior of their lattice modes.

V. DISCUSSION

With these general principles in mind, we can begin to account for observed trends in mode-pressure sensitivity of our materials. First, however, we note an important point relating to the data themselves.

All our earlier work in the IR and Raman spectra of these materials¹⁻³ was done in a d. a. c. without gaskets, whereas the present work was done under more nearly hydrostatic conditions (see the introductory and experimental sections). There are very significant differences between the two sets of data. In particular, the shifts of the IR-active ν_3 mode of the anions were greatly underestimated in the earlier work. Thus, for K₂PtCl₆,

$\bar{\nu}_3$ (345 cm ⁻¹)	$\bar{\nu}_4$ (185 cm ⁻¹)	$\bar{\nu}_L$ (88 cm ⁻¹)	Ref.
0.35,	0.80,	0.90,	2,
0.62,	0.60,	0.76,	12,
0.81,	0.55,	0.70,	this work.

This serves to illustrate the importance of using gasketed, as opposed to ungasketed, d. a. c.'s.

Trends in pressure sensitivity

(i) *General.* Overall γ_i values tend to increase with decrease of $\bar{\nu}_i$ but there are many exceptions. The picture will become clearer when we are able to obtain far-IR spectra < 100 cm⁻¹ using gasketed d. a. c.'s, a matter of considerable experimental difficulty. At present our few reliable data on lattice mode pressure shifts are mostly from Raman spectra.

In all cases for which we have data, $\bar{\nu}_1 > \bar{\nu}_2$ but $\gamma_1 > \gamma_2$. However, γ_5 is invariably greater than γ_1 , γ_2 , and γ_3 , and $\bar{\nu}_5 < \bar{\nu}_1$, $\bar{\nu}_2$, $\bar{\nu}_3$. γ_4 is also usually, but not invariably, greater than γ_{1-3} . Nevertheless, our results cannot be said to provide support for Zallen's proposed relationship¹³ $\gamma_i \propto (\bar{\nu}_i)^{-2}$: A similar conclusion was reached by Wong.¹⁴ It must be added that Zallen studied molecular crystals, for which the relation might be valid.

(ii) *Grüneisen constants for individual compounds.* The observation that, for any one compound, γ_1 is invariably greater than γ_2 is helpful. For $\bar{\nu}_1$ and $\bar{\nu}_2$ the G -matrix elements are identical, but the force constants which govern $\bar{\nu}_1$ are greater than those for $\bar{\nu}_2$ (e. g., $K + 4F$ for $\bar{\nu}_1$, and $K + 0.7F$ for $\bar{\nu}_2$ in the Urey-Bradley force field).¹⁵ Hence $\bar{\nu}_1 > \bar{\nu}_2$.

For any one compound, r_0 in Eq. (5) is constant. Further, we note from Tables II and IV that $(d \ln \bar{\nu}_i / dP)_T$ and γ_i show identical trends. Hence, variations in γ_i are related to variations in $k_{\alpha\beta\gamma} / k_{\alpha\beta}^2$. We know that $k_{\alpha\beta\gamma} \dots$, for $\bar{\nu}_1$ is greater than that for $\bar{\nu}_2$: Hence, the order $\gamma_1 > \gamma_2$ must be determined by the greater value of the anharmonic force constant $k_{\alpha\beta\gamma}$ of $\bar{\nu}_1$.

(iii) K₂PtCl₆, Rb₂PtCl₆, and Cs₂PtCl₆. In accounting for trends in γ_i with change of compound we begin from a very simple model. Since the compressibility of each of these compounds is made up of contributions from both types of ion, the compressibility of a series of compounds with the same complex anion will vary in the order of the compressibilities of the individual cations. We assume that the latter increase with increase of atomic number within a given group: The compressibilities of rock-salt type alkali halides increase in the order NaCl, KCl, RbCl; NaBr, KBr, RbBr, etc.

TABLE IV. Mode Grüneisen parameters γ_i for complex halides A₂MX₆ calculated from the data of Tables II and III.

	$\bar{\nu}_1$	$\bar{\nu}_2$	$\bar{\nu}_3$	$\bar{\nu}_4$	$\bar{\nu}_5$	$\bar{\nu}_L$ (IR)
K ₂ PdCl ₆	0.32
K ₂ ReCl ₆	0.37	...	0.27	0.24	0.67	0.71
K ₂ OsCl ₆	0.41	0.27
K ₂ PtCl ₆	0.35	0.24	0.36	0.54	0.60	1.15 ~ 1.6 ^a
Rb ₂ PtCl ₆	0.30	0.21	0.21	0.39	0.68	...
Cs ₂ PtCl ₆	0.24	0.13	0.22	0.47	0.82	...
Tl ₂ PtCl ₆	0.22	0.25
K ₂ PtBr ₆	0.29	0.20	0.22	...	0.85	0.49 ^b
K ₂ SnCl ₆	0.40	0.38	0.37	0.34	0.63	...
Rb ₂ TeCl ₆	0.44	0.31	0.39	0.64	0.79	1.87 ^b

^aRefers to inactive lattice mode $t_{1g} \sim 60$ cm⁻¹, Ref. 35.^bRaman-active lattice mode.

In a series such as $A_2(PtCl_6)$ we therefore expect that, as A is varied from K to Rb to Cs, an increasingly large proportion of the applied stress will be used to compress the electron shells of the cations. Consequently, the effect on the internal modes of $(PtCl_6)^{2-}$ will be progressively less. This is exactly the trend observed for γ_i , $\Delta\bar{\nu}_i/\Delta P$, and $(d\ln\bar{\nu}_i/dP)_T$ for A_2PtCl_6 , with $A = K, Rb, Cs$ for $i = 1$ to 3 (i. e., the three Pt-Cl stretching modes) except for $\bar{\nu}_3$ (Rb).

Equation (5) may also be applied here. The Pt-Cl bond stretching force constants ($k_{\alpha\beta}$) are known to increase from Cs (~ 1.74) to Rb (~ 1.80) to K ($\sim 1.85 \times 10^2$ Nm^{-1}).¹⁶ The Pt-Cl bond lengths r_0 increase very slightly from 2.323 for K to 2.349 for Cs.^{10,17} From these data, $(r_0/k_{\alpha\beta})^2$ is seen to increase from K to Rb to Cs; however, $(d\ln\bar{\nu}_i/dP)_T$ follows the reverse trend for the Pt-Cl stretching modes ($i = 1$ to 3), implying that the trend is dominated by an increase in anharmonicity ($k_{\alpha\beta\gamma}$) from Cs to Rb to K salts.

For the bending modes $\bar{\nu}_4(t_{1u})$ and $\bar{\nu}_5(t_{2g})$, γ_i decreases from Cs* to K*, i. e., the reverse of the trend for the stretching modes, except for γ_4 of K_2PtCl_6 . The implication here is that the harmonic force constants are the major influence for the trend in γ_i for $\bar{\nu}_4$ and $\bar{\nu}_5$, rather than anharmonic force constants. This conjecture is supported by the knowledge that, at least for systems such as triatomics for which full potential constants have been evaluated, the stretch-stretch constants k_{rrr} and k_{rrrr} are at least an order of magnitude greater than all other cubic and quartic constants.¹⁸

Since completion of our work, Bretinger *et al.*¹⁹ have reported on the variation of $\Delta\bar{\nu}_i/\Delta P$ for the Raman-active modes of several salts of $(PtCl_6)^{2-}$ and $(PtBr_6)^{2-}$. For the chlorides, our data are broadly in agreement with theirs and show the same trends, except for their value for $\bar{\nu}_5$ of Cs_2PtCl_6 which may be in error. However, in our hands this compound photodecomposed in the laser beam when under pressure and the discrepancy may originate in this difficulty.

(iv) K_2PtBr_6 . Comparing K_2PtCl_6 with K_2PtBr_6 , for the Pt-halogen stretching modes $\bar{\nu}_1$ to $\bar{\nu}_3$, γ_i for the chloride is greater than for the bromide in each case (i. e., $i = 1$ to 3). The same is true for the analogous pairs of Rb and Cs salts.¹⁹

Again using Eq. (5), it appears that the differences in $(d\ln\bar{\nu}_i/dP)_T$ for the two materials arise because of greater anharmonicity in the chloride. Thus taking the known Pt-Cl (2.323 Å)¹⁷ and Pt-Br (2.463 Å)²⁰ distances, and the Pt-Cl (1.76) and Pt-Br (1.43×10^9 Nm^{-2}) bond stretching force constants,¹⁶ $(r_0/k_{\alpha\beta})^2$ is seen to increase substantially from K_2PtCl_6 to K_2PtBr_6 , whereas $(d\ln\bar{\nu}_i/dP)_T$ values are nearly identical for $i = 1$ to 3 for the two compounds (Table II). The difference in $(r_0/k_{\alpha\beta})^2$ must therefore be overlaid by a large opposite change in $k_{\alpha\beta\gamma}$, in order to account for the observed order of γ_i 's.

(v) *Nontransition metal complexes*. Extending the observations to the other salts shown in the tables, we note that almost all γ_i values for K_2SnCl_6 and Rb_2TeCl_6 are greater than those for transition metal salts. For the

Te case this is not surprising as there is known to be a nonbonding electron pair in an a_{1g} orbital around the metal atom which greatly reduces the Te-Cl bond stretching force constants below what would otherwise be expected.^{21,22} Both Te and Sn are "softer" than the Group VIII transition metal atoms.

For the Pd, Os, and Ir salts no Raman data were obtained, due to their deep colors. γ_3 for K_2PdCl_6 is 0.32 compared with 0.37 for K_2PtCl_6 , whereas $\bar{\nu}_3(Pd) > \bar{\nu}_3(Pt)$. From Eq. (5) this implies that the anharmonic contribution is more important in the Pd case.

(vi) *Possible phase transitions*. K_2SnCl_6 is unusual in showing an initial range of pressure insensitivity [Fig. 2(a)]. It is known that this material is near instability at ambient conditions^{23,24}; it has phase transitions at 263 and 255 K at ambient pressure which arise, basically, because K^+ is almost too small for the cavity it occupies.²⁶ Initially the rise in pressure results in a decrease in cavity size which is not reflected in any rise in anion internal mode frequencies. Subsequently, at about 5 kbars, the compound behaves normally.

There are clear indications of phase transitions in the $(CH_3)_4N^+$ salts, particularly for $(TeCl_6)^{2-}$ and $(SnCl_6)^{2-}$ [Figs. 2(b)-2(d)]. In both cases these are near 10 kbars. All three of these $(CH_3)_4N^+$ salts are known to show phase transitions with change of temperature at ambient pressure,²⁶⁻²⁸ almost certainly due to removal of methyl torsional disorder.²⁸

(vii) *Anharmonicity analysis*. Our pressure-shift data may be used to analyze the variation of mode frequency versus temperature data for K_2PtCl_6 and K_2ReCl_6 , according to Eq. (6)²⁹

$$\left(\frac{\partial \ln \bar{\nu}_i}{\partial T}\right)_P = \left(\frac{\partial \ln \bar{\nu}_i}{\partial T}\right)_V - \frac{\alpha}{\chi_T} \left(\frac{\partial \ln \bar{\nu}_i}{\partial P}\right)_T \quad (6)$$

The first term on the right-hand side is the volume-independent anharmonic self-energy term and the second term is the thermal strain shift. From our measured values of $\bar{\nu}_i$ versus either temperature or pressure $(\partial \ln \bar{\nu}_i/\partial P)_T$ and the total shift $(\partial \ln \bar{\nu}_i/\partial T)_P$ were estimated. To complete the calculation we need both the volume thermal expansion coefficient α and the isothermal volume compressibility χ_T for each compound.

Recent measurements³⁰ of $\alpha(111)$ for K_2ReCl_6 and K_2OsCl_6 up to 240 K and 220 K, respectively, extrapolated to 300 K, show that for both salts $\alpha(111)$ is $\sim 51 \times 10^{-6} K^{-1}$, corresponding to a volume thermal expansion coefficient $\alpha = 3[\alpha(111)/\sqrt{3}]$, of $88 \times 10^{-6} K^{-1}$. We assume, reasonably, that K_2PtCl_6 will also have the same value of α .

The calculated compressibilities χ_T for K_2ReCl_6 and K_2PtCl_6 differ by only $0.40 \times 10^{-6} bars^{-1}$ (Table III). Using the experimental value of χ_T for K_2ReCl_6 ($7.2 \times 10^{-6} bars^{-1}$), $\alpha/\chi_T = 12.3 bars K^{-1}$; taking $\chi_T = (7.2 - 0.4) \times 10^{-6} bars^{-1}$ for K_2PtCl_6 , we have $\alpha/\chi_T = 13.0 bars K^{-1}$. On this basis the thermal strain terms of Table V were calculated. We note that since these compounds are cubic, no qualifications arise due to anisotropy of α and χ_T .³¹

None of the values of the total shift (columns 2 and 3

TABLE V. Thermal strain and self-energy shifts for K_2ReCl_6 and K_2PtCl_6 . (All values are in units of $10^{-5} K^{-1}$.)

M =	Total shift ^a		Thermal strain		Self-energy	
	Re	Pt	Re	Pt	Re	Pt
$\tilde{\nu}_1, A_{1g}$	-1.4 ^b	-5.8	3.1	2.9	~1.7	-2.9
$\tilde{\nu}_2, E_g$...	-4.7	...	2.0	...	-2.7
$\tilde{\nu}_3, T_{1u}$	-7.4	-6.2	2.2	3.0	-5.7	-3.2
$\tilde{\nu}_4, T_{1u}$	+1.5	+2.6	2.0	4.4	3.5	7.0
$\tilde{\nu}_5, T_{2g}$	+8.3 ^b	+5.8	5.5	4.9	13.8	10.7
$\tilde{\nu}_L, T_{1u}$	~0	~0	5.9	9.5	5.9	9.5

^aSee Fig. 3.^bBased upon difference between values at room temperature (this work) and 6 K (Ref. 36, Fig. 15).

of Table V) are large (shifts of about $50 \times 10^{-5} K^{-1}$ are more typical in molecular crystals),³⁸ implying that the thermal strain and self-energy contributions are roughly equal and opposite. This is clearly the cause of the thermal insensitivity of the IR-active lattice mode.

$\tilde{\nu}_3$ is, however, quite significantly affected by change of temperature in the range 120 to 300 K, and for this mode the two terms reinforce each other. Here, as for the other M-Cl stretching modes [except for $\tilde{\nu}_1(Re)$], the self-energy term is negative. Since the self-energy term originates in a sum of two contributions, one of which depends solely upon quartic and the other upon both cubic and quartic anharmonicity,³² we conclude that the distinctive behavior of $\tilde{\nu}_3$ is to be associated with it having a different ratio of cubic to quartic anharmonicities from the other modes.

ACKNOWLEDGMENTS

We thank NATO for Research Grant No. 1245 which greatly assisted this collaboration, and the SRC for a grant (to ADW).

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