

ABSTRACT

LASER EXCITED FLUORESCENCE OF I_2 , RAMAN SPECTRA OF PERIODATE CRYSTALS,
AND RAMAN SPECTRA OF CRYSTALLINE ACETYLENE AND DEUTERATED ACETYLENE

By
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Three independent projects were performed. In the first, the laser excited (Ar^+ 5145 Å and HeNe 6328 Å) fluorescence spectra of iodine vapor were studied. It was found that the Ar^+ 5145 Å laser excited primarily the 43-0 P (12) and 43-0 R (14) transitions (with approximately equal intensity) with a small amount from a $v''=1$ state with a high rotational level ($J'' \gtrsim 100$). The HeNe 6328 Å laser excited primarily the 6-3 P (33) transition along with a small amount of the 11-5 R (127) transition. After these levels were laser resonance excited, a large number of additional excited states were generated by collisional processes before fluorescence. These appear to account for essentially all other features of the spectra.

In the study of the Raman spectra of periodate crystals, sodium, potassium, rubidium, silver and ammonium periodate powder crystals of the Scheelite (C_{4h}^6) structure were studied. $NaIO_4$ single crystals were analyzed for symmetry assignments which were carried to the other compounds by analogy. All samples were studied both at room temperature and $\sim 77^\circ K$. The shifts in periodate fundamentals were found to be dominated by an electrostatic (site) interaction potential. Five of the six Raman active lattice modes were observed

and symmetries assigned; however it appears that translations of both cations and anions as well as the librations of the anions are mixed (within symmetry blocks). Splittings on the two bending NH_4^+ ion fundamentals plus two additional lattice modes (NH_4^+ librations) verify that the NH_4^+ group does not rotate freely.

The Raman spectra of crystalline C_2H_2 and C_2D_2 were obtained to aid in the determination of the crystal structure of the lower temperature phase. In general, the D_{2h} factor group with two molecules per primitive cell on C_{2h} (1) sites interprets all spectral features, except ν_4 of C_2D_2 which has two additional unpredicted components. Mixed crystal spectra were also obtained where one isotope was matrix isolated in a host lattice of the other isotope. The spectral splittings were interpreted in terms of site and factor group terms, and intensity calculations were performed using the "oriental gas" model. The intensity calculations support an angle of $\sim 45^\circ$ between the molecular axis and the crystallographic z axis.

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LASER EXCITED RESONANCE FLUORESCENCE OF MOLECULAR IODINE

Introduction

The visible fluorescence spectrum of iodine vapor has been studied for more than fifty years.¹ This work has led to the accurate evaluation of the ground electronic state ($^1\Sigma_g^+$) vibration-rotation constants by Rank and Rao² and the first excited electronic state's ($^3\Pi_{Ou}+$) vibration-rotation constants by Steinfeld, *et al.*³ In addition to these studies, iodine has been used several times⁴ for the study of energy transfer processes in gases. To perform these studies, it was necessary to monochromatically excite the I_2 vapor, which was normally "quenched" by addition of a foreign gas. The development of the laser provided an ideal excitation source for such experiments.

Laser excited fluorescence has been reported for diatomic potassium⁵ and sodium,⁶ from which the vibration-rotation constants were determined to higher accuracy than were previously available. Concurrent with our study, the observation and identification of krypton ion ($5682 \text{ \AA}$) laser excited fluorescence of I_2 was reported,⁷ as well as observation of Ar^+ ($5145 \text{ \AA}$) laser excitation.^{8,9,10} Also, $6328 \text{ \AA}$ HeNe laser excited I_2 fluorescence was reported¹¹ and identified,¹² in complete agreement with our work. More recently, an analysis of the $5145 \text{ \AA}$ Ar^+ laser excited spectrum (and HeNe $6328 \text{ \AA}$ again) has been presented.¹³ However, it appears that one of

the Ar^+ laser excited transitions has been mislabeled, and the weak "anti-Stokes" one was not observed.

This work was originally initiated to study the Raman spectrum of ICN (and the series of cyanogen halides). However, irradiation of ICN with approximately 800 mwatts of $5145 \text{ \AA}$ laser radiation caused the solid ICN sample to decompose, forming gaseous iodine as one of the decomposition products. This iodine then absorbed the $5145 \text{ \AA}$ laser radiation, undergoing the transition from the $1\Sigma_g^+$ ground state to the $3\Pi_{0u}^+$ excited electronic state, and the more intense fluorescence spectrum of the I_2 vapor was recorded instead of the Raman spectrum of ICN. In the present study the first high resolution analyses of the $5145 \text{ \AA}$ Ar^+ and $6328 \text{ \AA}$ HeNe laser excited fluorescence spectra of I_2 were performed.

Interpretation

The expected fluorescence spectrum from monochromatically excited I_2 would consist of almost equally spaced doublets separated from each other by the ground state vibrational energy level spacings. The P-R doublet spacing (resulting from the $\Delta J = \pm 1$ selection rule for the fluorescence) would depend on the rotational quantum number J , the larger the J value the greater the separation. For a given J , the doublet's spacing would slowly decrease at higher vibrational quantum numbers v'' as a result of the vibration-rotation interaction terms in B_v'' . If, as is the case for I_2 , there are several transitions that overlap the excitation energy of the (nearly) monochromatic source, then

there will be a P-R doublet for each of these transitions; however, one component of each doublet will coincide at each vibrational level, for this will be the transition that overlapped the laser's energy for excitation and then fluoresced giving no overall change in rotational quantum number J . This results from the fact that the selection rule $\Delta J = \pm 1$ applies both upon excitation and fluorescence back to the ground state. Therefore the total ΔJ will be either 0 and +2 (for R excitation) or 0 and -2 (for P excitation). In either case, the $\Delta J_{\text{Total}} = 0$ transition will be allowed, and at each vibrational level of the fluorescence spectrum these components will again overlap since the energy differences involved are identical.

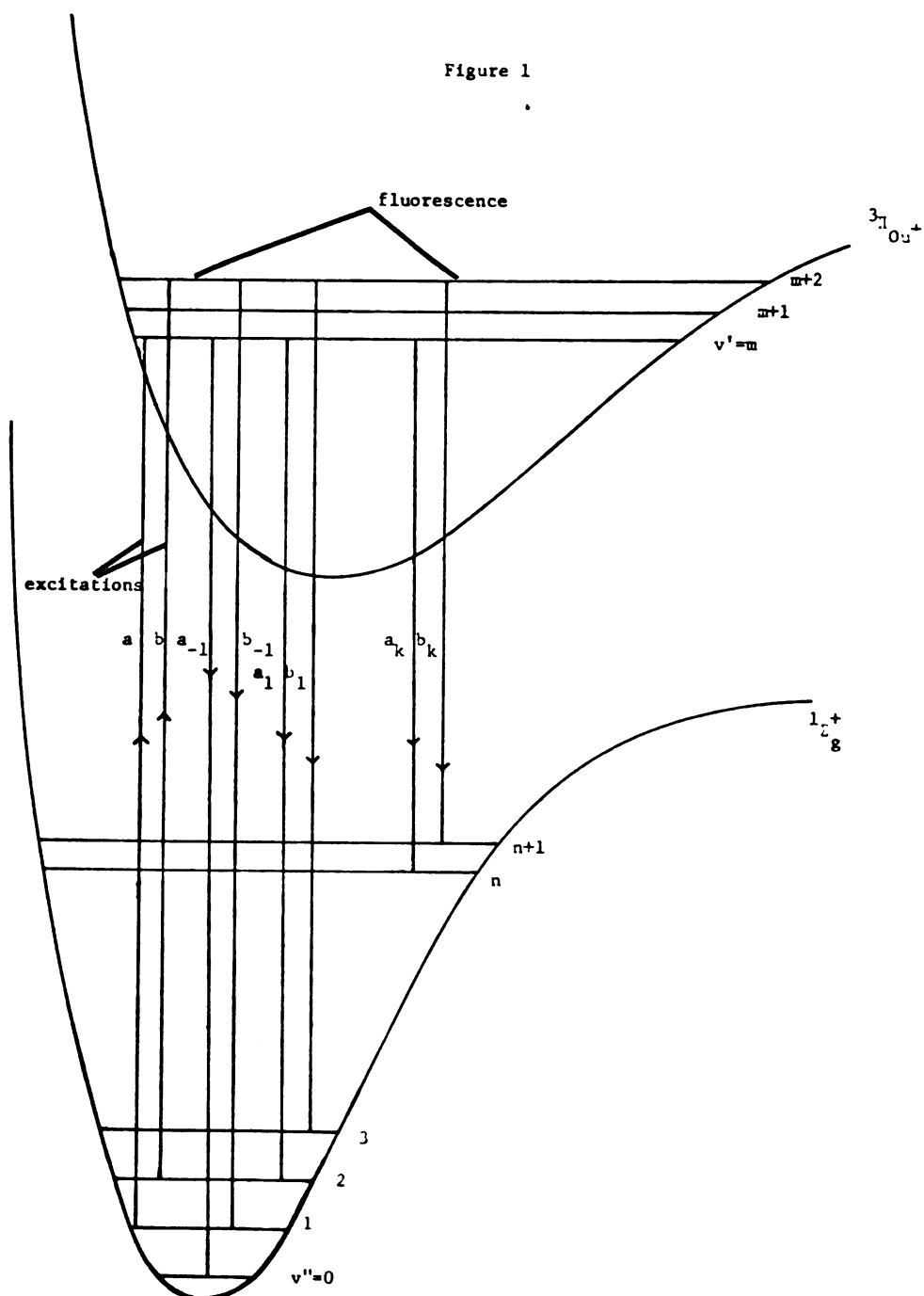
If, however, the two excitation transitions initiated in different vibrational levels of the ground state, when they fluoresce back to vibrational levels separated by the same difference in v'' the $\Delta J_{\text{Total}} = 0$ transitions will not be precisely overlapping, but rather will be separated by the anharmonicity of the ground state. Furthermore, as one progresses to higher and higher vibrational components of the fluorescence spectrum, this separation of the $\Delta J_{\text{Total}} = 0$ components increases, since the separation of the two transitions being excited remains the same, while at each higher vibrational energy level the anharmonicity causes the energy difference upon fluorescence to become smaller. Thus the $\Delta J_{\text{Total}} = 0$ transitions initiating in vibrational levels only one (or a few) quantum numbers apart will almost completely overlap in the first few vibrationally shifted components of the fluorescence spectrum, but will become completely resolved in the more highly shifted components.

This effect can most easily be visualized by viewing Figure 1 which shows two transitions (labeled a and b) being excited by the monochromatic source. a_1 and b_1 then represent the fluorescence back to the ground state with one vibrational quantum more in energy than the initial ground state. [This will in the future be referred to as the "1st Stokes" component.] Analogously, the a_k and b_k represent the "kth Stokes" component, or fluorescence back to the kth vibrational level above the level from which it was excited. And the fluorescences labeled a_{-1} and b_{-1} represent the first "anti-Stokes" component of the spectrum. These definitions of "Stokes" and "anti-Stokes" are not rigorously correct; however, they carry the same significance as in Raman spectroscopy and will simplify the remainder of the discussion. From Figure 1, one can clearly see that the $\Delta J_{\text{Total}}=0$ transitions of the first Stokes components of a and b will be nearly superimposed, while the kth Stokes components will now be quite different in energy. Also, as one progresses to higher and higher Stokes components, the $\Delta J_{\text{Total}}=0$ fluorescence that was excited from the higher ground vibrational level will shift to higher energies (shorter wavelengths) relative to the fluorescence excited from the lower ground vibrational level, while as one goes to higher and higher anti-Stokes components, the reverse happens.

Figure 1

The effect of anharmonicity on the I_2 fluorescence spectrum.
(schematic)

Figure 1



The final factor to consider in the interpretation of the I_2 spectra is the intensity of the various vibrational components of the fluorescence series. The intensities of the fluorescence from a particular vibrational level of the excited molecule to the various vibrational levels of the ground state are given by the Franck-Condon factors. These are just the overlap integrals of the vibrational wave functions for the respective ground and excited state vibrational energy levels. The Franck-Condon factors of interest for this analysis were calculated by the method developed by Zare¹⁴ and supplied to us by Prof. J. I. Steinfeld.¹⁵

Experimental

Reagent grade iodine (from Matheson, Coleman, and Bell) was used without further purification. The sample cell used was a small glass tube with flat (90°) windows and a side-arm U-tube that contained the solid iodine. The U-tube could be placed in an appropriate slush bath for temperature control. Initially the sample cell was fitted with a stopcock so that the cell could be evacuated (through a liquid N_2 trap) and then simply shut off. However, when the background pressure became of more importance, the cell was pumped down as before (only now to a background pressure of $\sim 5 \times 10^{-6}$ mm Hg) and sealed off under these conditions. Precise quantities of foreign gas could be admitted prior to seal-off, if desired.

The instrument used was a laser-Raman spectrometer¹⁶ consisting of: either a Spectra-Physics Model 125 HeNe laser (providing

~100 mwatts 6328 Å radiation) or a Spectra-Physics Model 140 Ar⁺ laser excitation source (providing, at optimum moments, nearly 1 watt of either 5145 Å or 4880 Å radiation); Spex 1400 double monochromator; ITT FW-130 "Startracker" selected grade S-20 photomultiplier tube; Victoreen VTE-1 D.C. amplifier; and Hewlett-Packard Moseley 7100 B strip chart recorder. In the final experiments, the Spectra-Physics Ar⁺ laser was replaced by a Coherent Radiation Model 52 Ar⁺ laser with essentially the same power output. The laser beam was focused into the sample by a lens (focal-length 10 cm) and then reflected by a concave mirror placed below the cell, thus approximately doubling the effective laser power. The fluorescence was collected at 90° from the laser's incident direction and focused on the monochromator entrance slit.

Results and Discussion

Table I lists the wavelength (in vacuum) of the central maximum ($\Delta J_{\text{Total}}=0$) of each vibrational level of the 5145 Å (~5146.77 Å in vacuum) Ar⁺ laser excited fluorescence spectrum that was obtained. Also listed are the total shifts in energy ($\Delta \nu_{\text{cm}}^{-1}$) from the exciting line and the separation of adjacent central maxima $\Delta(\Delta \nu_{\text{cm}}^{-1})$, along with the change in vibrational quantum number $\Delta v''$ and a literature value for $\Delta(\Delta \nu_{\text{cm}}^{-1})$.¹⁷ From this table it is clear that our instrumentation and hence our data are not of high enough accuracy to improve the quality of the already available constants for I₂. However, for the purpose of assigning the observed resonance fluorescence, enough accuracy was obtained to determine the most probable vibronic transitions occurring in our spectra.

Table I
 I_2 fluorescence data ($5145 \text{ \AA}^{\circ}$ excited)

$\lambda(\text{vac}) \text{ \AA}^{\circ a}$	$\Delta\nu(\text{cm}^{-1})$	$\Delta(\Delta\nu)(\text{cm}^{-1})$	$\Delta\nu''$	$\text{Lit}\Delta(\Delta\nu)^b(\text{cm}^{-1})$
5204.08	213.99	213.99	1	213.31
5262.55	428.52	214.53	2	212.05
5321.25	637.10	208.58	3	210.80
5381.26	846.66	209.56	4	209.66
5442.60	1056.08	209.42	5	208.50
5504.26	1261.92	205.84	6	207.20
5567.30	1467.63	205.71	7	205.80
5631.53	1672.49	204.86	8	204.55
5696.76	1875.93	203.44	9	203.18
5763.14	2078.02	202.09	10	201.93
5830.20	2277.59	199.57	11	200.68
5898.75	2478.12	200.53	12	199.30
5968.30	2674.49	196.37	13	198.05
6039.60	2872.29	197.80	14	196.73
6111.60	3067.34	195.05	15	195.36
6184.75	3260.87	193.53	16	194.06
6259.50	3453.95	193.08	17	192.73

- a. R.m.s. error on 38 readings for first 3 vibrational levels is $\pm 0.30 \text{ \AA}^{\circ} \rightarrow \pm 1.1 \text{ cm}^{-1}$ at $5145 \text{ \AA}^{\circ}$.
- b. Reference 17.

The possible transitions with energy approximately the same as either the 5145 Å Ar^+ or 6328 Å HeNe laser lines are listed in Table II. This table is excerpted from Steinfeld, et al.'s paper.¹⁸ (It should be noted that more recent work¹⁹ indicates an error in assignment of the 57-2 band as the 49-1 band. Therefore, the new, more accurate constants reported in ref. 18 are not an improvement over those of ref. 3. The earlier constants were used in our calculations.) The J'' values for the 45-0 and 50-1 transitions in Table II were increased by one from those reported by Steinfeld, et al. This was determined by a computer fit of the vibration-rotation constants^{2,3} for the transitions of interest. See Appendix I for details of these calculations and the results.

Figure 2 shows the highest resolution we could obtain for the "first Stokes" component (i.e. $v'' \xrightarrow{\text{laser excit.}} v' \xrightarrow{\text{fluorescence}} v'' + 1$) of the 5145 Å Ar^+ laser excited spectrum. The central peak (labeled a) corresponds to the rotationally unshifted ($\Delta J_{\text{Total}} = 0$) component of each transition initiating in the $v'' = 0$ ground state. The two other largest peaks (labeled b and c) correspond to the rotationally shifted components of the transitions 43-0 P(12) and 43-0 R(14) respectively. The peak labeled d could correspond to the rotationally shifted component of the 45-0 P(65) series. However, since it is comparable in size to the other small peaks further from the central peak which have been ascribed to a collisional process changing the energy level of the excited state of the molecule prior to fluorescence (see next paragraph), peak d is probably primarily one of these peaks. This has

Table II

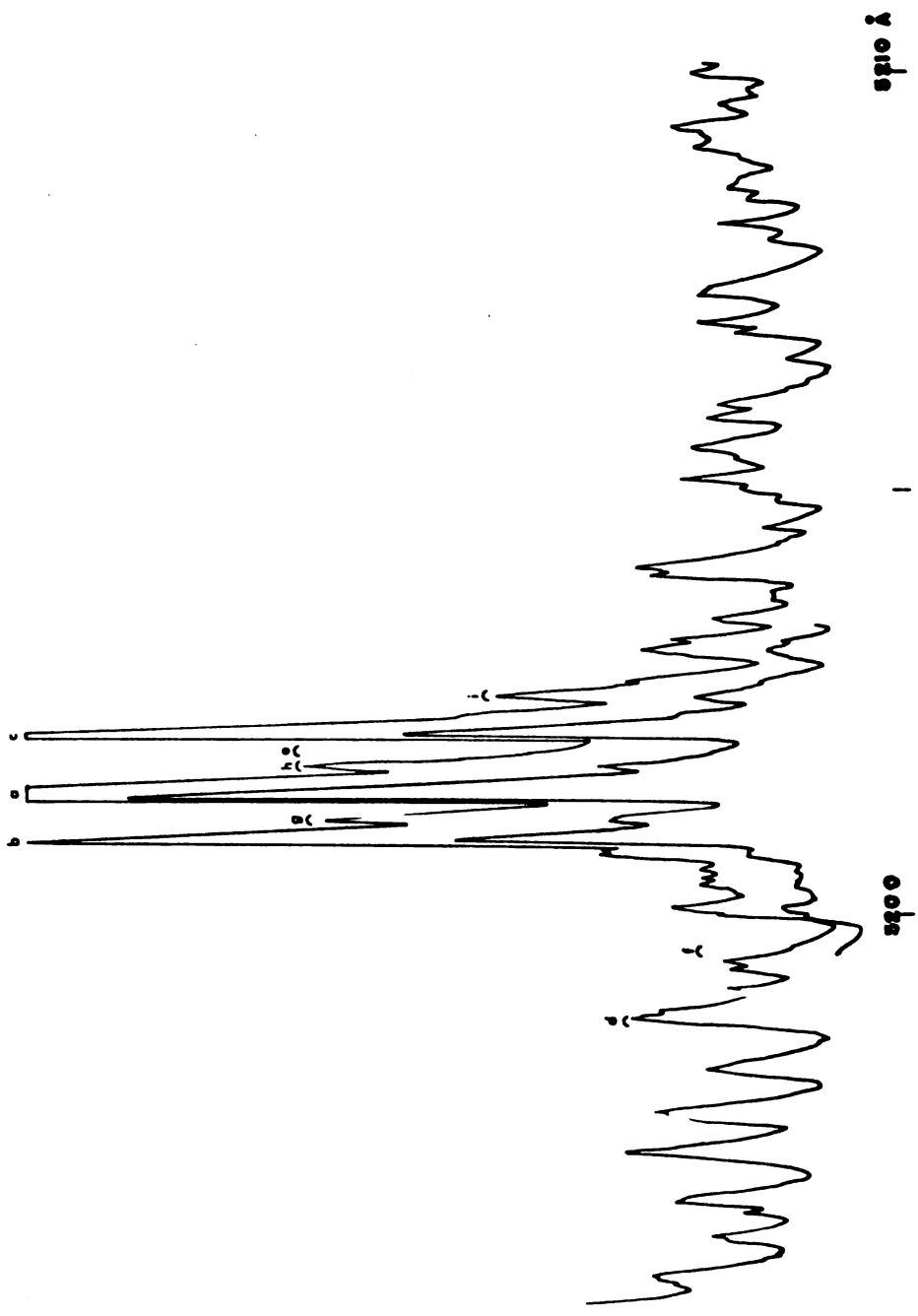
Transitions with energy coincidence with either HeNe 6328 Å or
 Ar^+ 5145 Å laser excitation.^a

	v'	v''	J''	$\lambda(\text{in air})$ associated with transition
Near 6328.16 Å (HeNe)	6	3	P(33)	6328.19 Å
	6	3	R(39)	6328.13
	9	4	P(119)	6328.11
Near 5145.36 Å (Ar^+)	43	0	P(12)	5145.379 Å
	43	0	R(14)	5145.384
	45	0	P(65)	5145.35
	49	1	R(18)	5145.43
	50	1	P(40)	5145.39

a. From reference 18, corrected as noted in text.

Figure 2

First Stokes fluorescence component of $\text{Ar}^+ 5145 \text{ \AA}$ laser excited spectrum of I_2 .



been confirmed by a later experiment [see Figure 9] which shows the I_2 fluorescence observed at -23°C where the vapor pressure is so low that the collisional background is much less intense. Positions labeled e and f correspond to the expected positions of the 50-1 P(40) doublet (e being separated from a by the anharmonicity of the ground state potential well).

An alternate explanation for some of the side peaks involves collisions while I_2 is in the excited state.⁴ Analogous to ortho and para hydrogen, an individual I_2 molecule possesses only all even or all odd J valued rotational levels. Also, the molecules in the proper ground state for $5145\text{ \AA}$ resonance excitation are very "poor" in rotational energy as can be seen from Figure 3. The requisite rotational quantum number $J''=12$ or 14 , and the most probable J'' value at room temperature is >50 . (Since $B' < B''$, J'_{max} will be $>J''_{\text{max}}$.) The actual temperature of the I_2 that is fluorescing is probably considerably higher than room temperature, since Holzer et al.⁹ found that bromine under similar experimental conditions absorbed so much energy from the laser beam that the temperature appeared to be approximately 700°K . This would change the rotational population to a distribution more like the dotted line of Figure 3, where J''_{max} is even higher.

Under these conditions, the most probable result of a collision yielding a minimal change in energy of an excited molecule will be to increase the rotational quantum number by two.⁴ Thus,

Figure 3

Boltzmann distribution of rotational energy levels of the ground electronic state of I_2 at 300°K and 700°K.

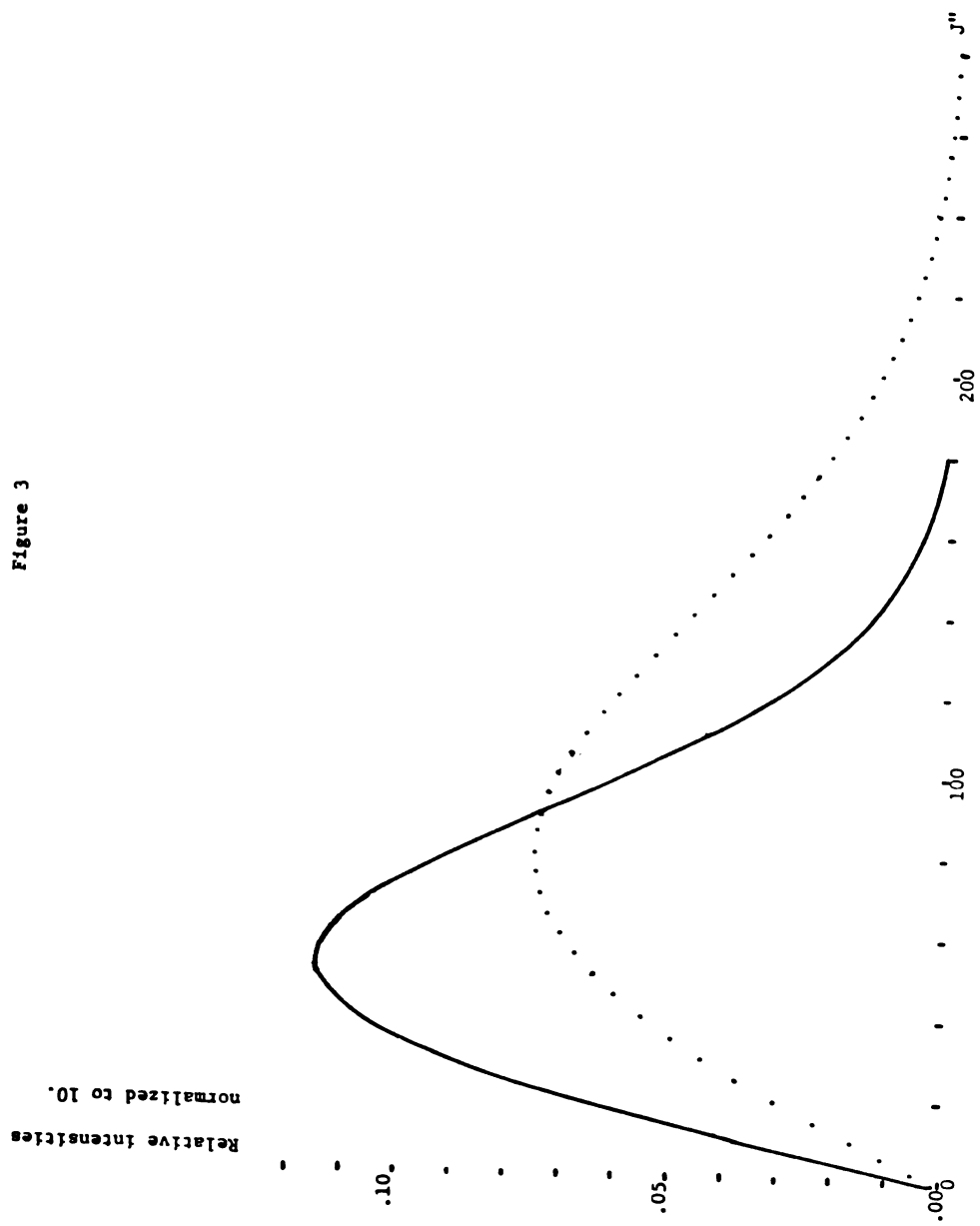


Figure 3

assuming this series of events: $v''J'' \xrightarrow[\text{excit.}]{\text{laser}} v'J' \xrightarrow{\text{collision}} v'$
 $(J'+2) \xrightarrow{\text{fluorescence}} v'' (J'+1)$ and $v'' (J'+3)$, we obtain the
 transitions labeled g, h and i in Figure 2 by using $v''J''$ as $0'' 12''$
 and $0'' 14''$ respectively.

Confirmation of this assignment can be made by observing
 Figure 4, which shows the eighteenth Stokes component. At this
 point in the fluorescence series, the difference in separation between
 the 0 - 1st vibrational quantum levels and the 18 - 19 ones (see
 Figure 1) will be $>20 \text{ cm}^{-1}$, so that both components of a doublet
 initiating in $v''=1$ would be shifted to more than 20 cm^{-1} higher in
 energy than the fluorescence excited from $v''=0$. We see that the small
 peaks are still in the same relative position to the larger ones of
 the series as they were in the first Stokes spectrum (Figure 2);
 therefore they must all have initiated from the same ($v''=0$) level.
 There are no other nearby transitions initiating from the $v''=0$ level
 which coincide with the laser's energy, with appropriate doublet
 separation, so we conclude that a collision of the molecule while
 it was in the excited state must have occurred.

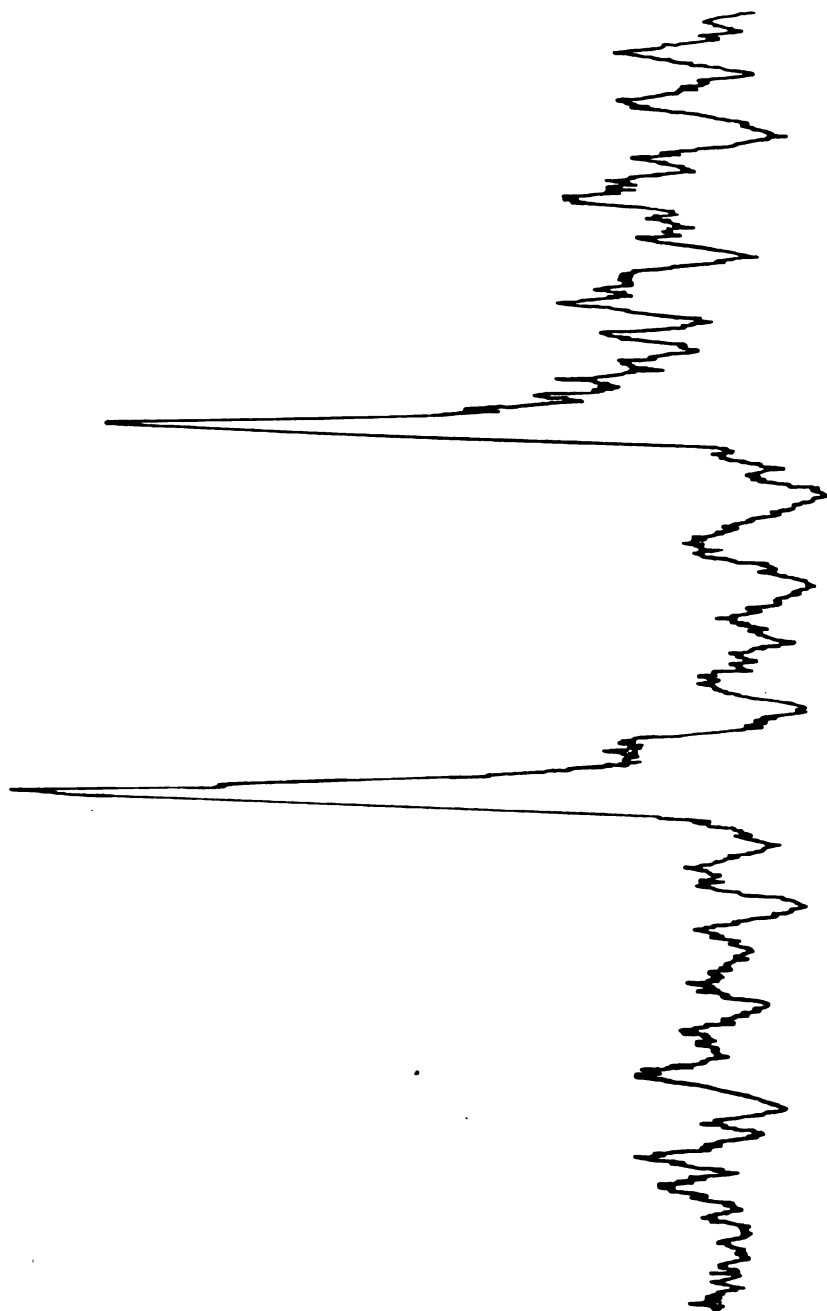
One can also separate the excitations starting in the
 $v''>0$ level from those starting in the $v''=0$ level by looking at
 the first anti-Stokes band ($v'' \rightarrow v''-1$), which has no analogous
 component in the series starting in $v''=0$. Figure 5 shows a scan of
 this region of the 5145 Å laser excited fluorescence spectrum, which
 consists of a widely spaced doublet. The wide splitting of this
 doublet implies a high rotational quantum number ($J'' \sim 100$), and to
 fit this with the laser's energy requires a transition to such

Figure 4
Eighteenth Stokes component of $\text{Ar}^+ 5145 \text{ \AA}$ laser excited
fluorescence of I_2 .

.

Figure 5

First anti-Stokes component of 5145 Å Ar^+ laser excited fluorescence of I_2 .



5088

5095 Å

a high vibrational level in the excited state that the experimental constants determined for low v' cannot be applied to determine the precise transition that occurred. This can be seen from the limits placed on the constants in ref. 18. The two transitions starting in $v''=1$ and the 45-0 transition listed in Table II, are not observed in our fluorescence spectra.

The HeNe 6328 Å laser excited spectrum consists predominantly of one transition, which, based upon its fit in energy, the rotational splitting of the doublets, and the order of magnitude of the corresponding Franck-Condon factors must be the 6-3 P(33) transition of Table II. Figure 6 shows the first two components of this series. At approximately 6447 Å and 6456 Å there are sudden increases in the non-resonance (collisionally shifted) fluorescence background. These are ascribed to collisions involving excited I_2 molecules that result in a loss of a vibrational quantum of energy before fluorescence. The first discontinuity arises from $v'=6 \rightarrow v'=5$. The second, less intense of these results from a much weaker fluorescence series, which is barely observable in the second Stokes component (near 6500 Å) in this region of the resonance spectrum. This weaker transition is clearly visible in Figure 7, which shows the 1st anti-Stokes, and 6th and 9th Stokes components of the fluorescence. This transition, although not listed in Table II, is best assigned as 11-5 R(127) as reported by Hanes and Dahlstrom.¹² A total of 5 anti-Stokes components were observed for this transition thus confirming that the excitation initiated in at least the 5th

Figure 6

First two Stokes components of HeNe 6328 Å laser excited
fluorescence of I₂.

Figure 7

First anti-Stokes, sixth and ninth Stokes components of
the 6328 Å laser excited fluorescence spectrum of I_2 .

vibrational level of the ground state. Again it appears highly likely that the I_2 is heated by the laser radiation. As can be seen in Figure 8, the population of the higher vibrational levels is significantly greater at higher temperatures. Unfortunately the potential constants for the excited state are not well enough known to calculate a vibrational temperature from the observed relative intensities of the $v''=3$ and $v''=5$ fluorescence series.

The relevant Franck-Condon factors for the fluorescence transitions observed in this work are listed in Table III.^{14,15} It should be noted that there is a significantly greater change in the magnitude of the individual v'' Franck-Condon factors for $v'=6$ fluorescence ($6328 \text{ \AA}^{\circ}$ excitation) than for the $v'\sim 43$ range ($5145 \text{ \AA}^{\circ}$ excitation). This larger, order of magnitude difference in the overlap integrals is reproduced in the observed intensities (Table IV); however even in this region the agreement is not excellent. All experimental intensities have been corrected for instrumental sensitivity (see Appendix II). In the higher ($v'\sim 43$) region, the calculated Franck-Condon factors are rather independent of v'' (see Table III), showing only a small parity dependence and no order of magnitude change over a large number of ground vibrational energy levels. Since even in the lower ($6328 \text{ \AA}^{\circ}$ excited) region, the Franck-Condon factors are not accurate enough to predict more than the order of magnitude of the intensities, it appears that the Franck-Condon factors are too insensitive to predict the relative intensities of

Figure 8

Boltzmann distribution of vibrational energy levels of the ground electronic state of I_2 at 300°K and 700°K.

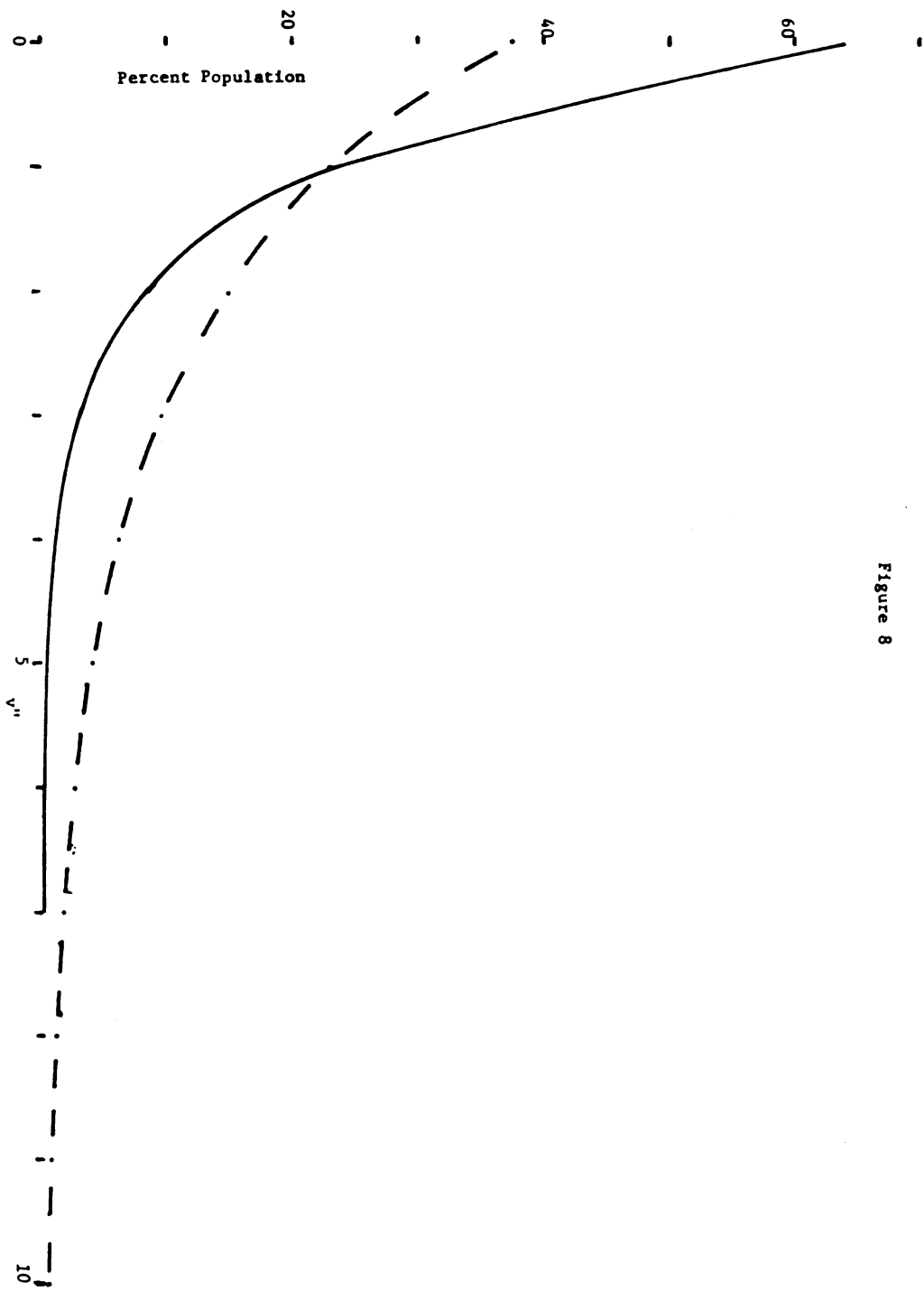


Figure 8

Table III
 Franck-Condon factors calculated by Zare's¹⁴ method, supplied by Prof. J. I. Steinfeld.¹⁵

v''	v'	6	...	41	42	43	44	45	46	47	48	49	50
0		.000024	.01827	.01878	.01772	.01683	.01620	.01197	.01116	.01041	.00941	.00888	
1		.000346	.00121	.00245	.00305	.00366	.00434	.00264	.00283	.00314	.00316	.00328	
2		.002306	.00893	.00687	.00576	.00475	.00387	.00418	.00358	.00288	.00237	.00202	
3		.009242	.00174	.00234	.00285	.00328	.00368	.00367	.00387	.00403	.00396	.00402	
4		.02455		.00514	.00411	.00321	.00246			.00080	.00051	.00029	
5		.04443		.00266	.00326	.00378	.00423			.00457	.00461	.00441	
6		.05337		.00423	.00317	.00227	.00154			.00021	.00005	.000000	
7		.03771		.00287	.00355	.00409	.00453			.00453	.00438	.00397	
8		.009483		.00367	.00259	.00170	.00102			.00003	.000003	.00007	
9		.001066		.00294	.00371	.00431	.00476			.00461	.00439	.00393	
10		.02121		.00328	.00218	.00129	.00065			.00001	.00013	.00034	
11		.03630		.00279	.00362	.00425	.00470			.00431	.00397	.00339	
12		.02063		.00308	.00196	.00107	.00046			.00009	.00031	.00060	
13		.000665		.00246	.00334	.00401	.00447			.00398	.00358	.00298	
14		.01087		.00309	.00193	.00101	.00038			.00018	.00048	.00085	
15		.03207		.00204	.00296	.00368	.00417			.00362	.00317	.00253	
16		.02523		.00330	.00208	.00109	.00041			.00020	.00054	.00093	
17		.002915		.00161	.00258	.00338	.00393			.00343	.00295	.00230	
18		.006379		.00364	.00237	.00128	.00051			.00019	.00055	.00096	
19		.02957		.00122	.00222	.00311	.00376			.00337	.00287	.00219	

Table III (cont.)

20	.03035	.00402	.00272	.00154	.00066	.00017	.00053	.00095
21	.007397	.00084	.00186	.00284	.00361	.00342	.00291	.00221
22	.002217	.00436	.00309	.00184	.00083	.00014	.00051	.00096
23	.02512	.00049	.00146	.00251	.00341	.00346	.00295	.00223
24	.03786	.00463	.00347	.00217	.00105	.00011	.00047	.00095
25	.01951	.00020	.00102	.00210	.00310	.00348	.00299	.00225

Table IV
 Observed intensities of 6328 Å and 5145 Å laser excited fluorescence
 spectra of I₂.

v''	5145 Å Intensity ^a	6328 Å Intensity ^b
0	coincident with laser	unobserved (<0.000)
1	.00305	unobserved (<0.000)
2	.00564	.00251
3	.00351	coincident with laser
4	.00337	.02455
5	.00300	.04115
6	.00154	.05074
7	.00259	.04516
8	.000967	.00550
9	.00293	
10	.000846	
11	.00217	
12	.000792	
13	.00178	
14	.000604	
15	.00143	
16	.000565	
17	.00134	
18	.000435	
19	.000891	
20	.000426	
21	.000536	
22	.000344	
23	.000350	
24	.000421	
25	.000273	

a. Normalized to $v'' = 1$ Franck-Condon factor of Table III.

b. Normalized to $v'' = 4$ Franck-Condon factor of Table III.

the transitions excited by the $5145 \text{ \AA}$ radiation. Thus our measured intensities (Table IV) probably give the relative Franck-Condon factors more accurately than those in Table III, which are calculated values.

Additional interesting information that can be obtained from our spectra concerns quenching. To quantitatively study the energy transfer peaks, better resolution than we are able to get of each multiplet is needed. However, an approximate estimate of collisional transfer probabilities can be obtained by studying the I_2 fluorescence as a function of temperature. Figure 9 shows the one anti-Stokes and first two Stokes components of the $5145 \text{ \AA}$ excited spectrum run at three different temperatures (21°C , 0°C and -23°C). The vapor pressure of I_2 at 20°C is 198.8 microns and at 0°C is 29.81 microns, while at -23°C extrapolation of Gerry and Gillespie's²⁰ data shows it to be not more than a few microns. The instrumental gain was varied for the different temperatures, but for one temperature the intensities were recorded at the same sensitivity. Figure 10 shows the quenching effect of 180 microns of He added to the cell with I_2 at room temperature. A definite increase in the intensities of post-collision fluorescence is observed. This aspect of our study was not pursued further, since it was felt to lie outside the immediate research interests of our group. However, these last spectra (Figures 9 and 10) along with a number of others have been supplied to Prof. J. I. Steinfeld for further investigation and analysis which will, hopefully, provide a better understanding of iodine quenching.

Figure 9

First anti-Stokes and first two Stokes components of $\text{Ar}^+ 5145 \text{ \AA}$
laser excited fluorescence of I_2 at 21° , 0° and -23°C .

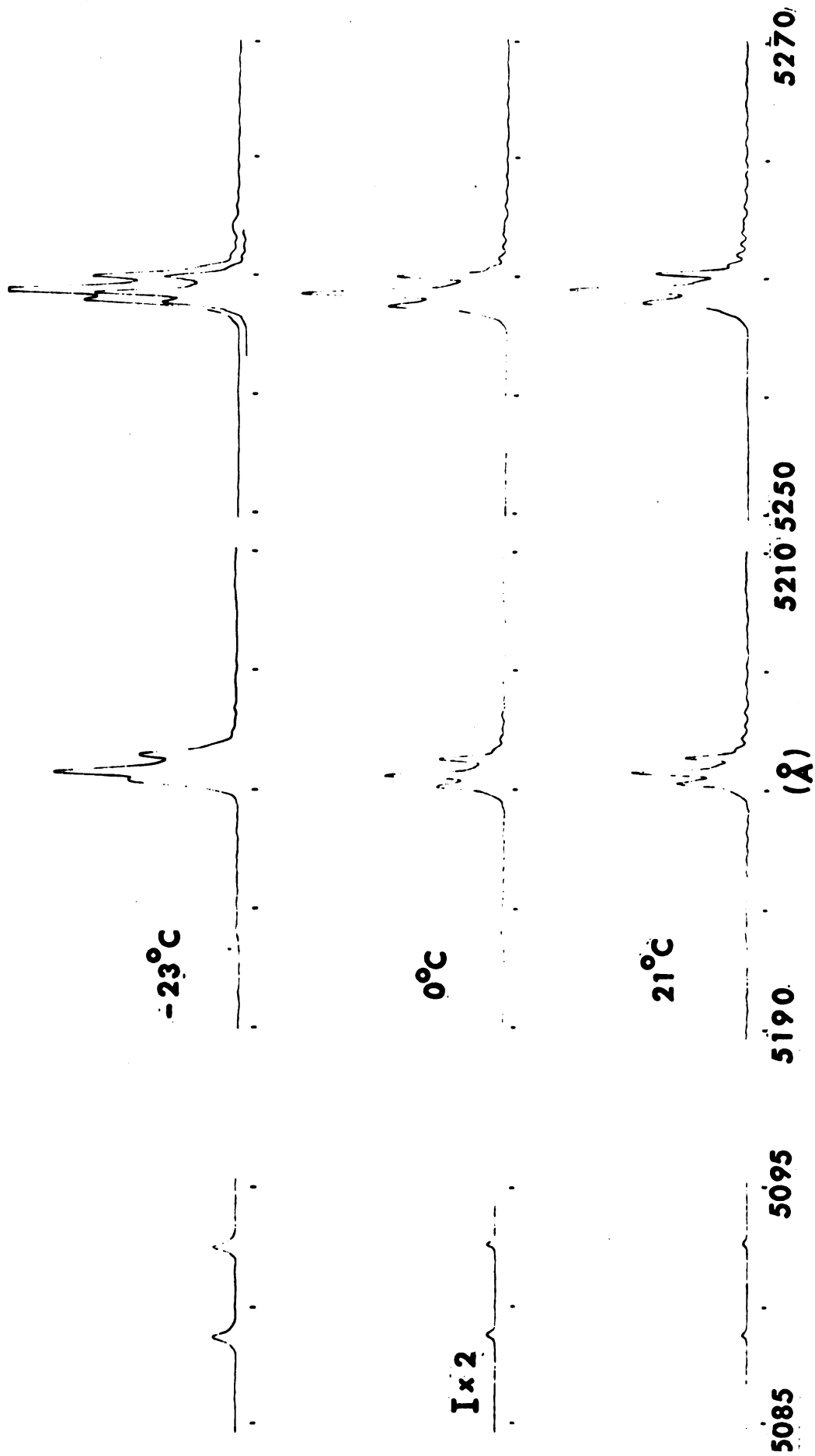
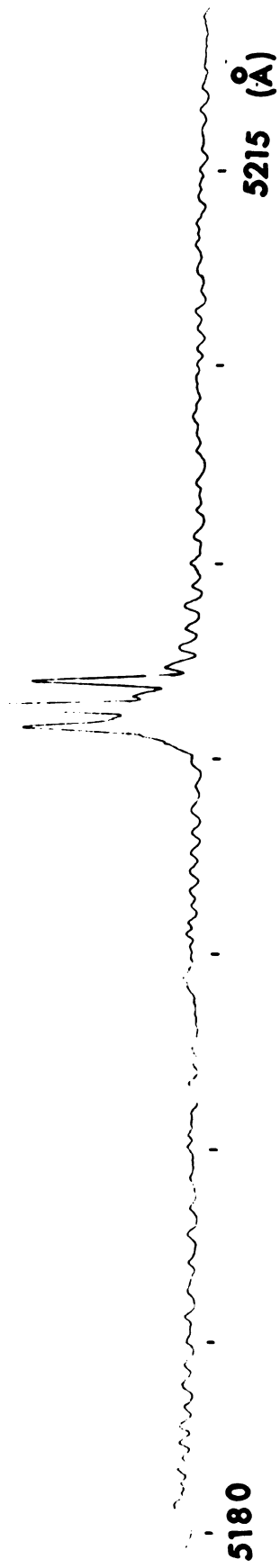


Figure 10

First anti-Stokes and first two Stokes components of $\text{Ar}^+ 5145 \text{ \AA}$ laser excited fluorescence of I_2 at 21°C with 180 microns of He gas added.

21°C

(+180 microns He)



Conclusions

We find almost all of the Ar^+ (5145 Å) laser resonance-excited fluorescence of I_2 to be due to the $43+0$ excitation. Of this $\sim 47\%$ is in the P(12) line and $\sim 53\%$ in the R(14) transition. The remaining small contribution ($< \sim 3\%$ total fluorescence intensity), is due to an unidentified excitation from a $J'' > \sim 100$, $v'' = 1$ level. Each of these excited states then gives rise to a whole series of other excited states by means of collisions before the molecule fluoresces. The other transitions of Table II which appear to match the laser's frequency were not excited with any observable intensity. The HeNe 6328 Å laser line resonance-excited primarily ($> \sim 90\%$) the 6-3 P(33) transition, with the remainder being the 11-5 R(127) transition. The other calculated fits were not observed. The Ar^+ 5017 Å laser line appeared to excite some transitions to even higher vibrational levels (v') than the 5145 Å line; however, this resonance excitation was not pursued since the published constants for the excited electronic state are not accurate enough to predict which specific transition was being excited.

The Franck-Condon factors calculated by Zare¹⁴ appear to work well in the HeNe 6328 Å case, where the intensities vary by more than an order of magnitude over just a few vibrational levels. However, they do not appear accurate enough at levels as high as $v' = 43$ to predict the intensities of the fluorescence components. This is due in part to the small changes in the values of the Franck-Condon factors over a rather extended number of vibrational levels and also to the inaccuracies in the parameters used to obtain the Franck-Condon factors.

Appendices I and II

APPENDIX I

Calculation of the Transition Energies of I_2

Following the respective conventions of references 2 (' state) and 3 (' state), one can write

$$G''(v'') = \omega_e''(v'' + \frac{1}{2}) + x_e \omega_e''(v'' + \frac{1}{2})^2 + y_e \omega_e''(v'' + \frac{1}{2})^3 \\ + z_e \omega_e''(v'' + \frac{1}{2})^4 + t_e \omega_e''(v'' + \frac{1}{2})^5$$

$$G'(v') = \omega_e'(v' + \frac{1}{2}) - \omega_e x_e'(v' + \frac{1}{2})^2 + \omega_e y_e'(v' + \frac{1}{2})^3 + \omega_e z_e'(v' + \frac{1}{2})^4$$

$$F''(J''-1) = [B_e'' + \alpha_e''(v'' + \frac{1}{2}) + \gamma_e''(v'' + \frac{1}{2})^2 + \delta_e''(v'' + \frac{1}{2})^3 \\ + \phi_e''(v'' + \frac{1}{2})^4] J''(J''-1) \\ + [D_e'' + \beta_e''(v'' + \frac{1}{2})] (J'')^2 (J''^2 - 1)$$

$$F'(J') = [B_e' - \alpha_e'(v' + \frac{1}{2}) + \gamma_e'(v' + \frac{1}{2})^2 + \delta_e'(v' + \frac{1}{2})^3] J'(J'+1) \\ - [D_e' + \beta_e'(v' + \frac{1}{2})] (J')^2 (J'+1)^2$$

where $G''(v'')$ is the vibrational energy of the ground ($^1\Sigma_g^+$) electronic state; v'' the ground vibrational quantum number; $G'(v')$ the vibrational energy of the first excited ($^3\Pi_{Ou}^+$) electronic state; v' the excited state's vibrational quantum number; $F''(J''-1)$ the rotational energy of the molecule in the ground electronic state and in the $J''-1$ rotational level [note that $F''(J''-1)$ is also a function of v'']; and

$F'(J')$ the rotational energy of the molecule in the excited electronic state in the J' rotational level [also a function of v']. The two electronic potential minima are separated in energy by the value T_e .

The potential constants are then given in Table V. The energy difference for a transition between the two electronic states is then given by

$$E = T_e + G'(v') - G''(v'') + F'(J') - F''(J'').$$

The selection rule $\Delta J = \pm 1$ applies, so $J' = J'' \pm 1$.

A computer fit was performed for transitions near those listed for 5145 Å^o excitation in Table II, using these equations and the constants given in Table V. The results are listed in Table VI. No additional fit was obtained to accurately assign the one anti-Stokes transition observed; however, this requires extending the potential constants for the excited electronic state beyond their accuracy limits, and it appears they were not applicable in this region.

Table V

Potential constants for ground ($^1\Sigma_g^+$) and first excited ($^3\Pi_{Ou}^+$) electronic states of I_2 . (all units are cm^{-1})

$T_e = 15770.59^b$		
Constant	Ground (") State ^a	Excited (') State ^b
ω_e	214.51886	125.273
$x_e \omega_e$	-0.60738	0.7016
$y_e \omega_e$	-1.307×10^{-3}	-5.67×10^{-3}
$z_e \omega_e$	-5.04×10^{-6}	$+3.2 \times 10^{-5}$
$t_e \omega_e$	-1.6×10^{-7}	
B_e	0.037389	0.028969
α_e	-1.210×10^{-4}	1.562×10^{-4}
γ_e	1.90×10^{-8}	-4.0×10^{-7}
δ_e	8.57×10^{-11}	-3.5×10^{-8}
ϕ_e	-1.86×10^{-10}	
D_e	-4.54×10^{-9}	3.5×10^{-9}
β_e	-1.20×10^{-11}	3.9×10^{-10}

a. Reference 2.

b. Reference 3.

Table VI

Calculated energies associated with transitions of I_2 near
 Ar^+ 5145 Å laser exciting line.

Laser Line Energy = 19429.66 cm^{-1} ($\sim 1 \text{ cm}^{-1}$ wide)			
$v''=0 - v'=43$		$v''=0 - v'=43$	
P transitions		R transitions	
J''	ΔE	J''	ΔE
10	19430.35	12	19430.40
11	19429.92	13	19429.96
12	19429.44	14	19429.49
13	19428.93	15	19428.98
14	19428.38	16	19428.44
$v''=0 - v'=45$		$v''=1 - v'=50$	
P transitions		P transitions	
J''	ΔE	J''	ΔE
		37	19434.40
63	19434.74	38	19432.78
64	19432.27	39	19431.13
65	19429.76	40	19429.43
66	19427.21	41	19427.70
$v''=1 - v'=49$			
R transitions			
J''	ΔE		
16	19431.20		
17	19430.54		
18	19429.84		
19	19429.10		
20	19428.32		
21	19427.50		

APPENDIX II

Intensity Calibration

The procedure for intensity calibration of the monochromator follows directly from the article by Stair, et al.²¹ The only difference in our calibration lamp's circuit from that of Figure 3 of ref. 21 is that a 0.60 ohm resistor was used in place of the ammeter so that one simply has to measure the voltage drop across the resistor to determine the current (0.60 volts/amp). A General Electric (GE) Model 6.6A/T4/CL 200-watt quartz-iodine lamp was used as recommended in ref. 21. Operating the lamp at 6.50 amps provided a filament color temperature measured to be 3060°K as expected. The temperature was measured using an optical pyrometer loaned to us by Dr. Eick's research group.

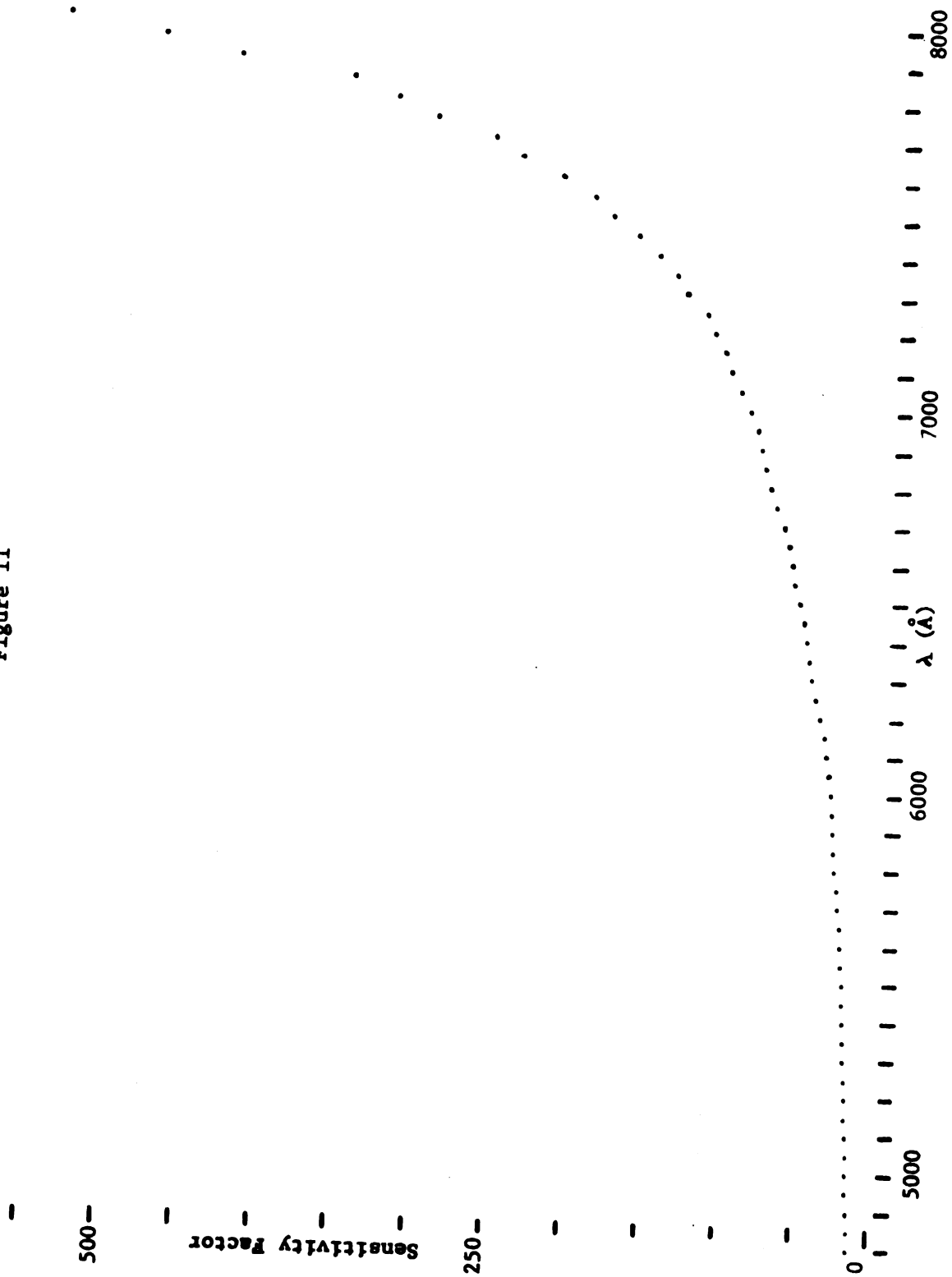
Figure 11 gives the intensity calibration obtained between 4800 Å and 8000 Å. This is a plot of sensitivity factor vs. wavelength (λ). The sensitivity factor is defined so that:

$$\text{sensitivity factor} \times \text{measured intensity} = \text{true relative intensity.}$$

Figure 11

Intensity calibration of laser-Raman spectrometer.

Figure 11



RAMAN SPECTRA OF PERIODATE CRYSTALS OF THE SCHEELITE STRUCTURE

Introduction

In the study of vibrational spectroscopy of crystals, the two principal goals are to determine crystal structures (where they are difficult to determine from diffraction experiments) from group theoretical analyses of the vibrational degrees of freedom, and to determine the nature of the intermolecular forces that dominate in the crystal. With the aid of single crystals unambiguous assignment of the symmetry of each vibrational motion observed can be made. By studying a series of similar compounds, one can hope to correlate the differences in the observed spectra with the differences in the forces in the corresponding crystals.

In this project, sodium, potassium, rubidium, silver and ammonium periodate powders were studied at room temperatures and cooled to approximately liquid N₂ temperatures. Also, several single crystals of NaIO₄ were studied. From the data obtained we assign the spectra, interpret the dominant intermolecular forces in these crystals, and also provide information to aid in the interpretation of the temperature dependence of their nuclear quadrupole resonance spectra.

Interpretation

The group theoretical treatment of the vibrational motions in crystals has been thoroughly developed.^{22,23} This is the so-called

"factor group" analysis, which first considers the isolated molecular (or ionic) point group in order to assign symmetries to the internal vibrational degrees of freedom and also to define the symmetries of the translations (T_x, T_y and T_z) and rotations (R_x, R_y and R_z) of the molecule as a whole. Then the point symmetry of the crystallographic site on which the molecule (or ion) is located is used to determine to which irreducible representations of this site group the symmetry coordinates of the molecule (molecular point group) belong. One can thus see if any molecular degeneracy is lifted at the site. (The site is usually of lower symmetry than the molecule.) Finally, these symmetry coordinates of the site are coupled to the other equivalent symmetry coordinates of the remaining sites of the primitive unit cell to form the symmetry coordinates of the factor group (unit cell group). From this we are able to predict the number of components of each of the internal vibrational fundamentals as well as the number of external (translational and librational) motions that will be active in both infrared and Raman spectroscopy. A more detailed explanation of the factor group analysis is included in Appendix III.

The appropriate factor group analysis for the periodates of the Scheelite structure is shown in Table VII. The crystallographic unit cell for the Scheelite structure is shown in Figure 12. Symmetry coordinate representations of the internal degrees of freedom of the tetrahedral IO_4^- group are given in Figure 13.²⁴ Scheelite has the C_{4h}^6 ($I4_1/a$) space group with two molecules per primitive unit cell, with both cations and anions on S_4 sites.²⁵ We then expect the Raman spectrum to consist of: 1(A_g) component of ν_1 , 2(A_g and B_g) components

Table VII

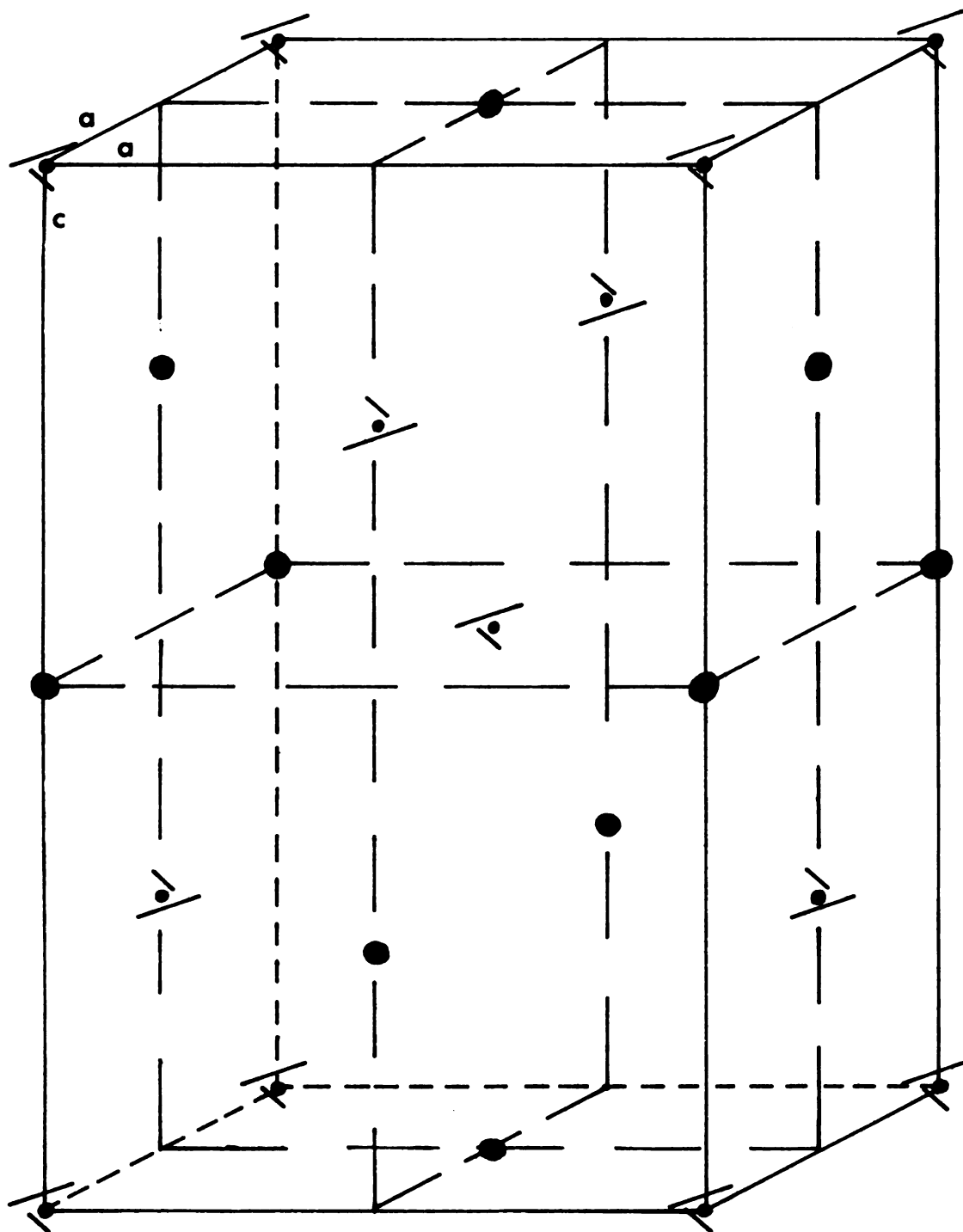
Correlation diagram for crystals of the Scheelite structure.

Molecular (anion) group	Site Symmetry	Factor Group Symmetry	Activity
<u>T_d</u>	<u>S₄</u>	<u>C_{4h}</u>	
ν_1	A ₁	A _g B _u	x^2+y^2, z^2 inactive
ν_2	E	B _g A _u	x^2-y^2, xy z (1 acoustic)
$(R_x, R_y, R_z)_{\text{anion}}$	T ₁	E _g E _u	(xz, yz) (x, y) (1 acoustic)
$\nu_3, \nu_4,$	T ₂		
$(T_x, T_y, T_z)_{\text{anion}}$			
$(T_x, T_y, T_z)_{\text{cation}}^a$			

^a Although the cations are not of symmetry T_d (except for NH₄⁺), they are on identical symmetry sites (S₄) and therefore their translational degrees of freedom behave identically to those of the anion.

Figure 12

Crystallographic unit cell for Scheelite structure.

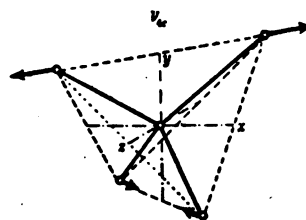
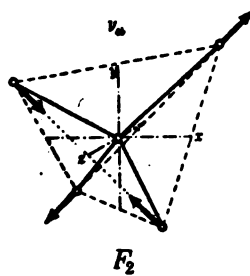
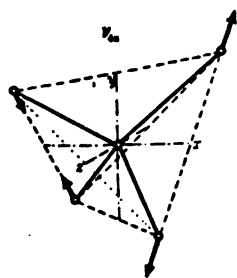
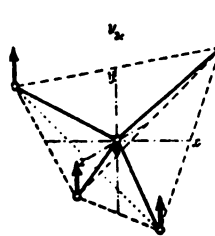
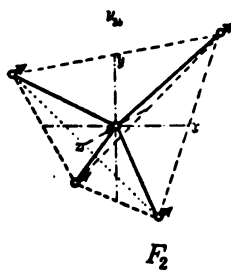
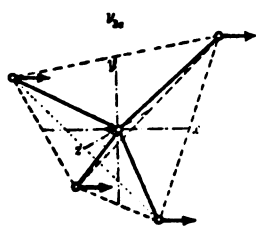
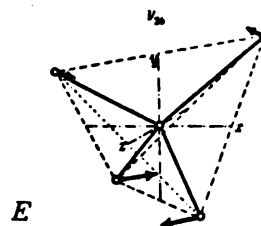
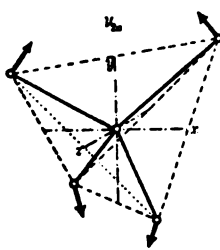
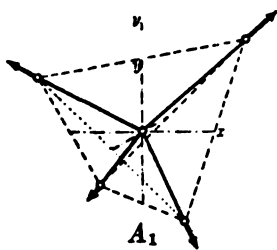


● = metal⁺ ion

● = 10_4^- ion

Figure 13

Symmetry coordinates for tetrahedral IO_4^- group, $F_2 = T_2$.



of ν_2 , 2(B_g and E_g) components each of ν_3 and ν_4 , and two librational (A_g and E_g) and four translational (2 B_g and 2 E_g) lattice modes. The infrared spectrum would consist of: 1 (A_u) component of ν_2 , 2(A_u and E_u) components each of ν_3 and ν_4 , and one librational (E_u) and two translational (A_u and E_u) lattice modes.

The frequencies of the various components of the internal degrees of freedom of the IO_4^- group will differ through the series of periodate crystals studied in this work because of the different interionic distances and forces. For example, $\nu_1(A_g)$ of the IO_4^- ion is found to vary in frequency from a low of 753 cm^{-1} in $AgIO_4$ to a high of 797 cm^{-1} in $RbIO_4$. If one can determine the general form of the interaction which dominates (if indeed one does dominate), then there should be a correlation between the frequency of the respective fundamentals and the relative magnitude of the interacting force for the different crystals.

Two basic models have been proposed for the interaction forces in crystals of the Scheelite structure.^{26,27} J. F. Scott²⁶ treated Ca^{++} , Sr^{++} and $Ba^{++}WO_4$, which had been subject to earlier spectroscopic investigation,^{28,29,30} and predicted the spectrum of $ZnWO_4$ by using a van der Waals' interaction force between nearest neighbor anions. This model is an extension of the multipole interaction model developed by Decius³¹ from the work of Mandel and Mazur.^{32,33} For the Raman spectrum, Scott²⁶ suggests that the dominant interaction term in the potential function between adjacent anions is the van der Waals' term which varies as $R_{\text{anion-anion}}^{-6}$. If one assumes that this

perturbing potential affects the internal force constants of the isolated periodate anion in the manner³⁴ $f_{\text{crystal}} = f_{\text{isolated anion}} + f'(V(R))$ where f' is the perturbation of the force constant due to the potential $V(R)$, and then assumes $f'(V(R)) = k \cdot V(R) + \dots$, i.e., the leading term in the perturbing force constant is proportional to the perturbing potential, we find that a plot of the square of the internal vibrational frequency vs. $R_{\text{anion-anion}}^{-6}$ would be expected to give a straight line. A similar plot (however, of frequency instead of frequency squared) for the tungstates was performed by Scott in ref. 26. It should be noted that if we separate the crystalline intermolecular interactions into two categories:^{35,36} the site effect due to electrostatic interactions in the crystal and factor group coupling due to resonance interactions of adjacent identical molecular (or ionic) groups in the crystal, Scott's model is based on the assumption that the perturbing potential causing the shift in internal frequency for the anion in the different crystals is due primarily to the change in the factor group coupling (Davydov splitting) strength between the various crystals in the series.

An alternative model for predicting the shift in fundamental frequency based on the change in magnitude of the site interaction in the series of crystals has been used by Ulbricht and Kriegsmann²⁷ for analysis of the perhenates of the Scheelite structure. In this model, the perturbation potential is assumed to be ionic and thus depend on $r_{\text{anion-cation}}^{-1}$. An additional parameter is necessary to specify the degree of ionic character of the crystal, which will vary

from cation to cation. A measure of the amount of ionic character can be obtained from the difference in electronegativity between the anion and cation. Unfortunately, the electronegativity of the IO_4^- is not known. If it were, one could take the difference in electronegativity between the cation and anion, square it to get a value proportional to the positive-negative ionic charge interaction, and divide by $r_{\text{anion-cation}}$ to obtain the relative perturbing potential functions. Since the electronegativity of the ReO_4^- ion was also not known, Ulbricht and Kriegsman simply used the electronegativity of the cation as a measure of the ionic character of the crystal.

Also, instead of assuming the force constant f to be dependent upon the perturbing potential according to the functional form $f'(V(r)) = k V(r)$ as Scott had done, they plotted the frequency versus the first derivative (force) of the potential. It has also been suggested by L. C. Kravitz³⁷ that the second derivative of the potential should be proportional to the shift in frequency of the fundamental. This is in analogy to calculating the harmonic force constant for a potential function. We are uncertain which of these plots (frequency vs zeroth, first or second derivative of the potential function) should give a linear relationship even if the assumed potential function is the correct one, and literature can be cited to support each.^{26,27,34,37}

We would also suggest that one should plot the square of the frequency vs some form of the potential function, since a perturbation on the force constant perturbs the square of the frequency; however, none of the above references does this. The limited data points that

we have obtained and the crudeness of both models make it impossible for us to determine experimentally which is correct. All types of plots mentioned above will be discussed in the Results and Discussion section, and it is clear that there exists enough difference between the two potential function forms to distinguish which type of potential dominates.

The external lattice vibrations are rather hard to classify beyond symmetry, since there are three degrees of freedom forming E_g symmetry modes $[(R_x, R_y)$ of anion, (T_x, T_y) of anion and cation] and two of B_g symmetry (T_z) of anion and cation). Only the A_g (R_z) of anion mode is of a unique symmetry. As a result, the normal coordinates of E_g and B_g symmetry can be an arbitrary mixture of the different degrees of freedom of the same symmetry. In addition, ν_4 , the lowest-lying fundamental of the IO_4^- group is so close in frequency to the external lattice frequencies that the normally-assumed separation of internal from external vibrations is likely also not to be valid.^{29,30,38,39} However, a knowledge of which particular frequency might best represent the libration of the IO_4^- group about the x and y axes (R_x, R_y) would be of particular interest for interpreting the temperature dependence of the NQR spectra of the periodate crystals.

If we can make some approximate assignment of the lattice modes, it would have to be by comparison of the frequency dependence in the series of crystals. If the vibrational mode is translational in origin and the translations of the cations and anions are independent of each other, the frequency of one E_g and one B_g motion should vary in

proportion to the inverse square root of the mass of the cation, and similarly one E_g and one B_g mode should be independent of the cation mass. At the other extreme, the Born-Von Karman model, if the cation and anion translations are totally coupled, there should be two E_g and two B_g modes whose frequencies vary as the reduced mass of the two ions. A mass dependence between these two could result from any partial mixture of the proper symmetry motions of the anions and cations. The dependence of the frequency on the dimensions of the unit cell [i.e., E_g proportional to a^2 (the x and y dimension), and B_g proportional to c (the z dimension)] is not as straightforward, since the cause of the change in unit cell size will be the change in cation which will be accompanied by a corresponding change in cationic radius. Therefore, the full effect of the change in the unit cell size will not be felt by the periodate group.

The librational motions of the periodate groups, if unmixed with the translational modes, should be relatively independent of the cationic mass, but depend on the cation electronegativity (i.e., covalent character). The R_z (A_g) motion is symmetrically unique, and it has been suggested that the other librational motion (E_g) be the E_g mode lying closest to the A_g mode,⁴⁰ since in cubic symmetry they would become degenerate.

Considerable work has been done on the study of rotational degrees of freedom of the NH_4^+ group in crystals, and

the phase transitions associated with the NH_4^+ motions.^{41,42,43,44} It has been concluded^{41,42} that rotational motion occurs in the warmer phases of the ammonium halide crystals; however, the exact nature of this motion is not completely understood.⁴³ For this reason we were interested in observing the fundamentals of the NH_4^+ group in NH_4IO_4 . If both site and factor group couplings are observed for the NH_4^+ fundamentals then it must not rotate, since the NH_4^+ must maintain one configuration long enough so that the environment does not average out during the molecular vibration. Furthermore the adjacent NH_4^+ ions must remain in one specific orientation with respect to each other for factor group coupling to occur. However, in our case, (T_d ion on S_4 site in C_{4h} factor group) all the fundamentals that are expected to give more than one component (ν_2 , ν_3 and ν_4) are already split by the site. Therefore restricted rotational motion (as long as it is not free rotation that would average the site effect out entirely) can still occur even with observation of splitting of the NH_4^+ fundamentals.

Experimental

Sodium, potassium, silver and ammonium periodate powders were obtained by Mr. Richard A. Johnson from Prof. M. T. Rogers and used without further purification. RbIO_4 was synthesized by Mr. Johnson from rubidium hydroxide and periodic acid, and the final product provided a white powder with sharp Raman spectra (completely analogous IO_4^- fundamentals) and no unpredicted peaks.

The single crystals of NaIO_4 were grown by Mr. Johnson by recrystallization from saturated aqueous solution by the procedure recommended by Kirkpatrick and Dickinson.⁴⁵

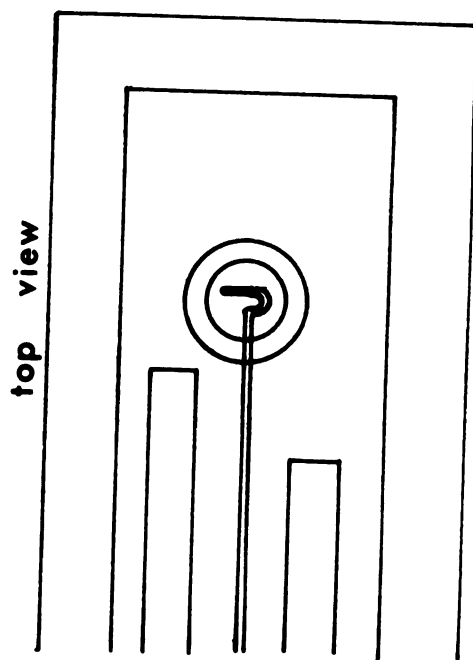
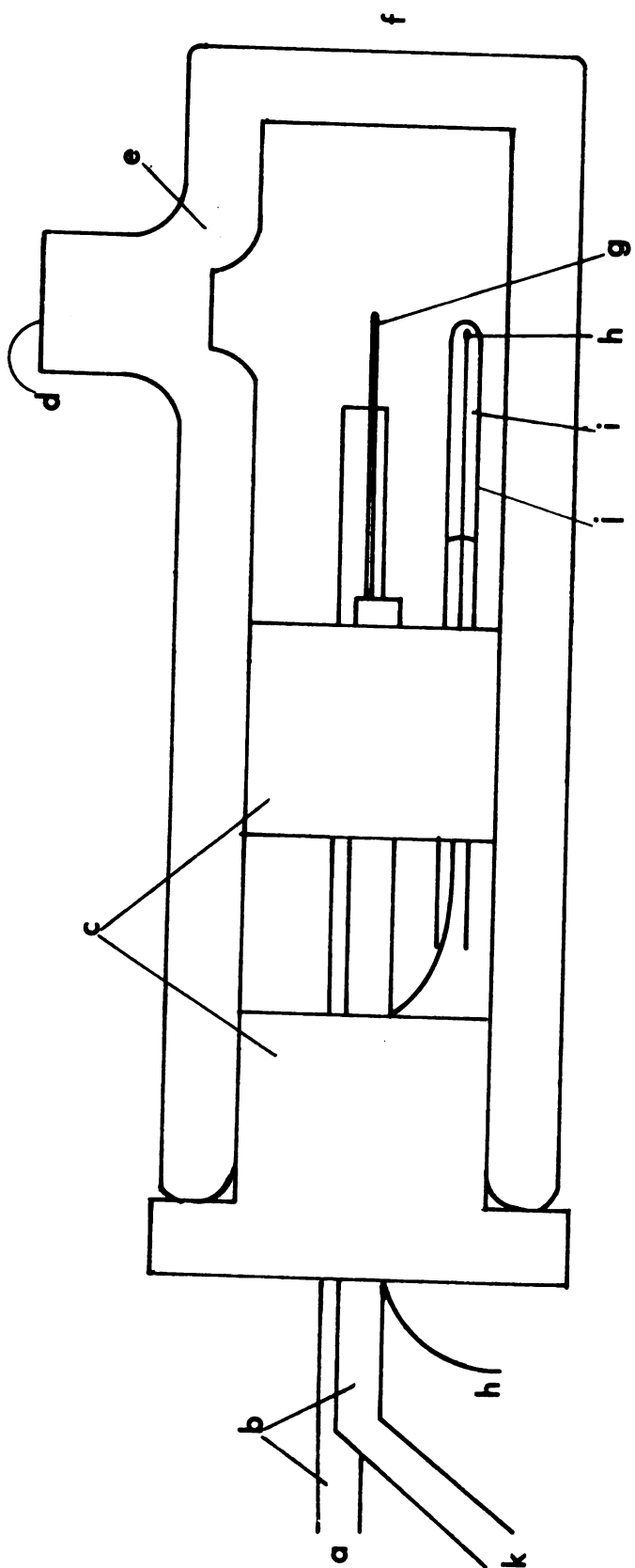
The Raman spectrometer used was that described in the previous chapter (see I_2 Fluorescence Experimental). Powdered samples were placed in bent capillary tubes which were mounted in an unsilvered dewar cell, as depicted in Figure 14. Nitrogen gas was passed through coils immersed in a liquid nitrogen reservoir and blown into the sample dewar for cooling. The flow rate of the N_2 gas, which could be accurately controlled, determined the temperature, which was measured by a Copper-Constantan thermocouple placed in a water-filled tube adjacent to the sample capillary. The single crystals of NaIO_4 were mounted on a goniometer in a glove box for room temperature spectra and attached by means of some clay to the end of a glass rod and placed in the dewar used for powder samples (Figure 14) for low temperature spectra.

Attempts were made to first determine the unique axis of the single crystals by means of optical polarization data (polarizing microscope) and it was found that the unique axis did not lie perpendicular to any of the crystal faces. Interfacial angles were then measured (using an optical microscope) and attempts were made to determine the unique axis from these; however, grinding and polishing the crystal to form a surface perpendicular to its c-axis resulted in loss of polarization of the Raman spectra and no significant increase in extinction under the polarizing microscope. As a result, the best

Figure 14

Unsilvered dewar for Raman spectra of solid samples.

- a. Inlet for cold N_2 from dewar.
- b. Insulated with 1/2" foam rubber tubing.
- c. Fitted cork stoppers.
- d. Window for laser exciting light.
- e. Evacuated glass jacket.
- f. Window for Raman scattered light.
- g. Bent capillary sample holder.
- h. Thermocouple.
- i. H_2O
- j. Glass tube
- k. N_2 outlet.



depolarization ratios (ratio of intensity of Raman scattering with polarization perpendicular to incident beam over intensity of Raman scattering with polarization parallel to incident beam) were obtained on two approximately perpendicular orientations of a crystal with uncut, unpolished surfaces. It might be noted that these NaIO_4 crystals were "home-grown" and as a result not as perfect and pure as professionally grown and oriented single crystals might be. Although the observed depolarization ratios are not numerically exactly in agreement with group theoretical predictions, enough accuracy was obtained to enable assignment of the symmetries of all the observed peaks in the NaIO_4 spectra. Assignment was carried to the other crystals by analogy.

Results and Discussion

Assignment of Symmetry

The frequencies of the internal IO_4^- vibrations in aqueous solution are known to be:⁴⁶

$$\begin{aligned}\nu_1(A_1) &= 793 \text{ cm}^{-1} \\ \nu_2(E) &= 272 \text{ cm}^{-1} \\ \nu_3(T_2) &= 854 \text{ cm}^{-1} \\ \nu_4(T_2) &= 310 \text{ cm}^{-1}\end{aligned}$$

From these frequencies and the correlation diagram for the Scheelite structure (Table VII), it is clear that with $\nu_1(A_g)$ and the two components of $\nu_3(B_g$ and $E_g)$ identified, the symmetries of the components of all the other vibrations in the crystal can be identified by comparison with the depolarization ratios of these three frequencies.

For C_{4h} symmetry, the following polarizability derivative matrices govern the Raman active intensities:⁴⁷

<u>C_{4h} Symmetry</u>	<u>Polarizability derivatives</u>
A_g	$\alpha_{xx} = \alpha_{yy} \neq \alpha_{zz}; \alpha_{ik} = 0$
B_g	$\alpha_{xx} = -\alpha_{yy} \neq \alpha_{xy}; \alpha_{iz} = 0$
E_g	$\alpha_{ii} = \alpha_{xy} = 0; \alpha_{yz} = \alpha_{xz}$

From these values, we see that the following spectra would be predicted: (See Table VIII). All other configurations simply reproduce these values.

With two approximately perpendicular orientations of a single crystal of $NaIO_4$ we were able to obtain (at $\approx 80^\circ K$) the depolarization ratios listed in Table IX. Figures 15 and 16 show the Raman spectra of the $NaIO_4$ single crystal in orientations 1 and 2 respectively. The small peak at $\approx 100 \text{ cm}^{-1}$ seen in Figure 15 in the "unanalyzed" portion of the spectrum on the low frequency shoulder of the second E_g lattice mode is a grating ghost.

Even with essentially perfect crystals, problems of internal reflection, birefringence, convergence and refraction limit the quality of polarization measurements so that the measured depolarization ratios are useful primarily to qualitatively assign symmetries. Thus, since we were able to accomplish the assignment of symmetries with our spectra, little could have been gained by the use of more perfect crystals. From our data (Table IX) it appears clear that orientation 1 was principally some mixture of orientations 1 and 3

Table VIII
Predicted intensities for polarized Raman spectra of NaIO_4 single crystal.

Orientations	Light entering along axis	Incident Polarization	Analyzer oriented to pass	Intensity		Analyzer	Intensity	Symmetry
					$\perp$			
1	z	x	x	α_{xx}		z	0	A _g
1	z	x	x	α_{xx}		z	0	B _g
1	z	x	x	0		z	α_{xz}	E _g
2	x	y	y	α_{xx}		x	0	A _g
2	x	y	y	α_{xx}		x	α_{xy}	B _g
2	x	y	y	0		x	0	E _g
3	x	z	z	α_{zz}		x	0	A _g
3	x	z	z	0		x	0	B _g
3	x	z	z	0		x	α_{xz}	E _g

Table IX

Depolarization Ratios ($\text{intensity}_{\perp} / \text{intensity}_{\parallel}$) for two orientations of an NaIO_4 single crystal at 81°K .

Assignment		Frequency (cm^{-1})	Orientation 1	Orientation 2
Lattice	B_g	97.7	1.04	1.92
	E_g	111.2	3.33	1.00
	E_g	153.1	4.17	1.43
	A_g	169.4	0.27	0.28
	E_g	218.3	4.55	1.03
ν_2	A_g	292.0	0.35	0.26
	B_g	301.5	0.35	1.47
ν_4	E_g	358.6	3.70	1.15
	B_g	377.0	1.27	2.13
ν_1	A_g	783.9	0.22	0.30
ν_3	E_g	832.3	5.00	1.01
	B_g	848.2	0.30	1.92

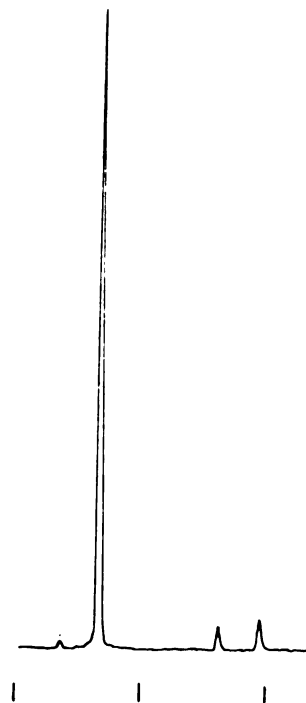
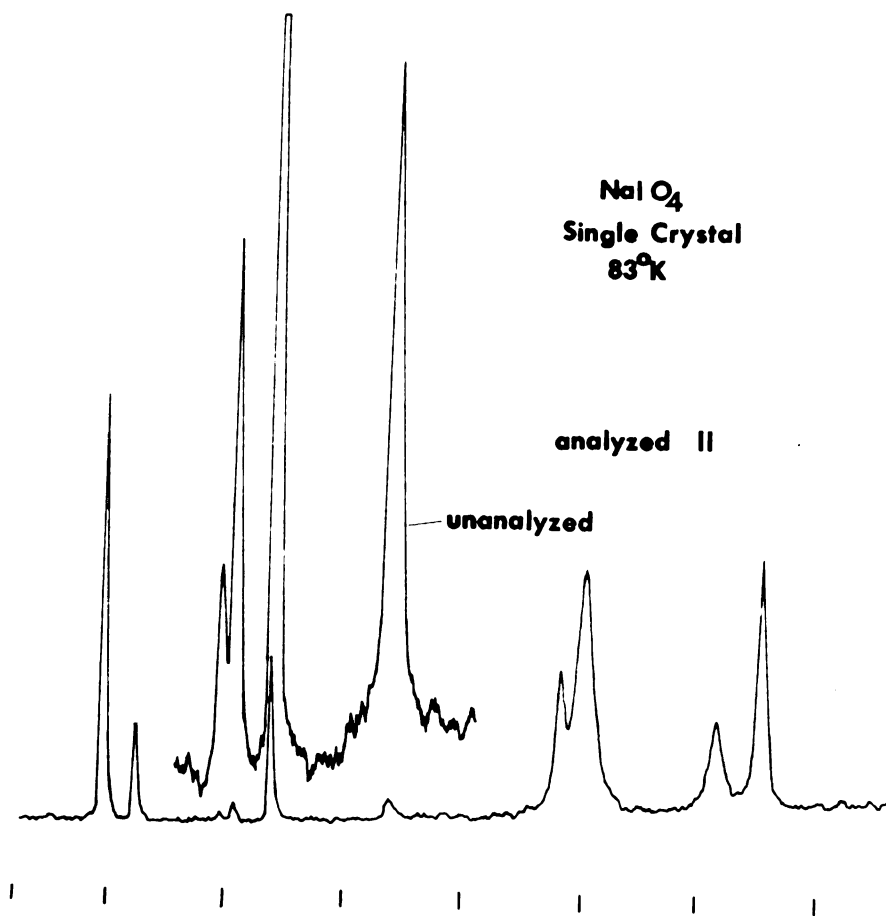
Figure 15

Raman spectrum of NaIO_4 single crystal in "orientation 1" at 83°K.

**NaI O_4
Single Crystal
83°K**

analyzed II

unanalyzed



analyzed I

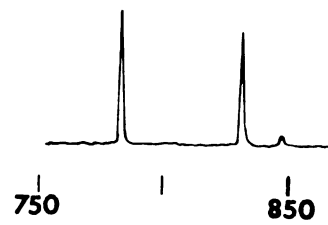
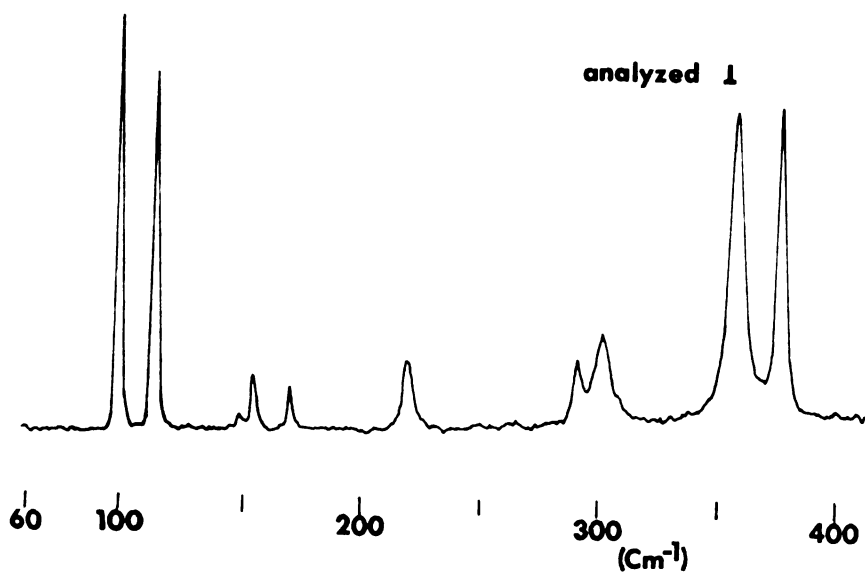


Figure 16

Raman spectrum of NaIO_4 single crystal in "orientation 2" at 97°K.

of the predicted intensities (Table VIII), while orientation 2 of Table IX is primarily orientation 2 of Table VIII.

Powder Spectra

The Raman spectra of Na^+ , K^+ , Rb^+ , Ag^+ and $\text{NH}_4^+\text{IO}_4^-$ at room temperature and approximately liquid nitrogen temperature are shown in Figures 17, 18, 19, 20 and 21 respectively, with the NH_4^+ fundamentals of NH_4IO_4 shown separately in Figure 22. Table X lists the Raman frequencies observed in this work, along with the infrared frequencies of reference 39 for the lattice region of the periodates at room temperature. Table XI lists the Raman lattice frequencies of the periodate crystals at approximately liquid nitrogen temperature. At most, five of the six predicted lattice modes were observed with certainty, with one B_g translational mode missing from all the spectra. Tables XII and XIII list the corresponding fundamental frequencies of the IO_4^- group at room and liquid nitrogen temperatures. The NaIO_4 (Figure 17) and RbIO_4 (Figure 19) spectra show no additional features than Tables X to XIII, except that RbIO_4 was later run under higher gain to show the highest frequency lattice mode. The KIO_4 spectrum (Figure 18) shows in addition to the data in Tables X to XIII, two weak, relatively broad peaks at $\sim 737 \text{ cm}^{-1}$ and 753 cm^{-1} , slightly lower in frequency (and less intense) than the O^{18} component of ν_1 . These might be assigned as combination bands of the infrared region of ν_4 ($398 + 338$ or 314 cm^{-1} , or $2 \times 398 \text{ cm}^{-1}$);³⁶ however, this would require rather large phonon dispersion curves. They are more likely impurity peaks, since the most probable impurity, IO_3^- , has Raman bands

Figure 17

Raman spectrum of NaIO_4 powder at 293° and 81°K.

Figure 18

Raman spectrum of KIO_4 powder at 293° and 100°K.

Figure 19

Raman spectrum of RbIO_4 powder at 293° and 80°K .

Figure 20

Raman spectrum of AgIO_4 powder at 293° and 80°K .

Peaks labelled G = grating ghosts

F = laser fluorescence lines

Ag_2O_2 Powder
293 °K

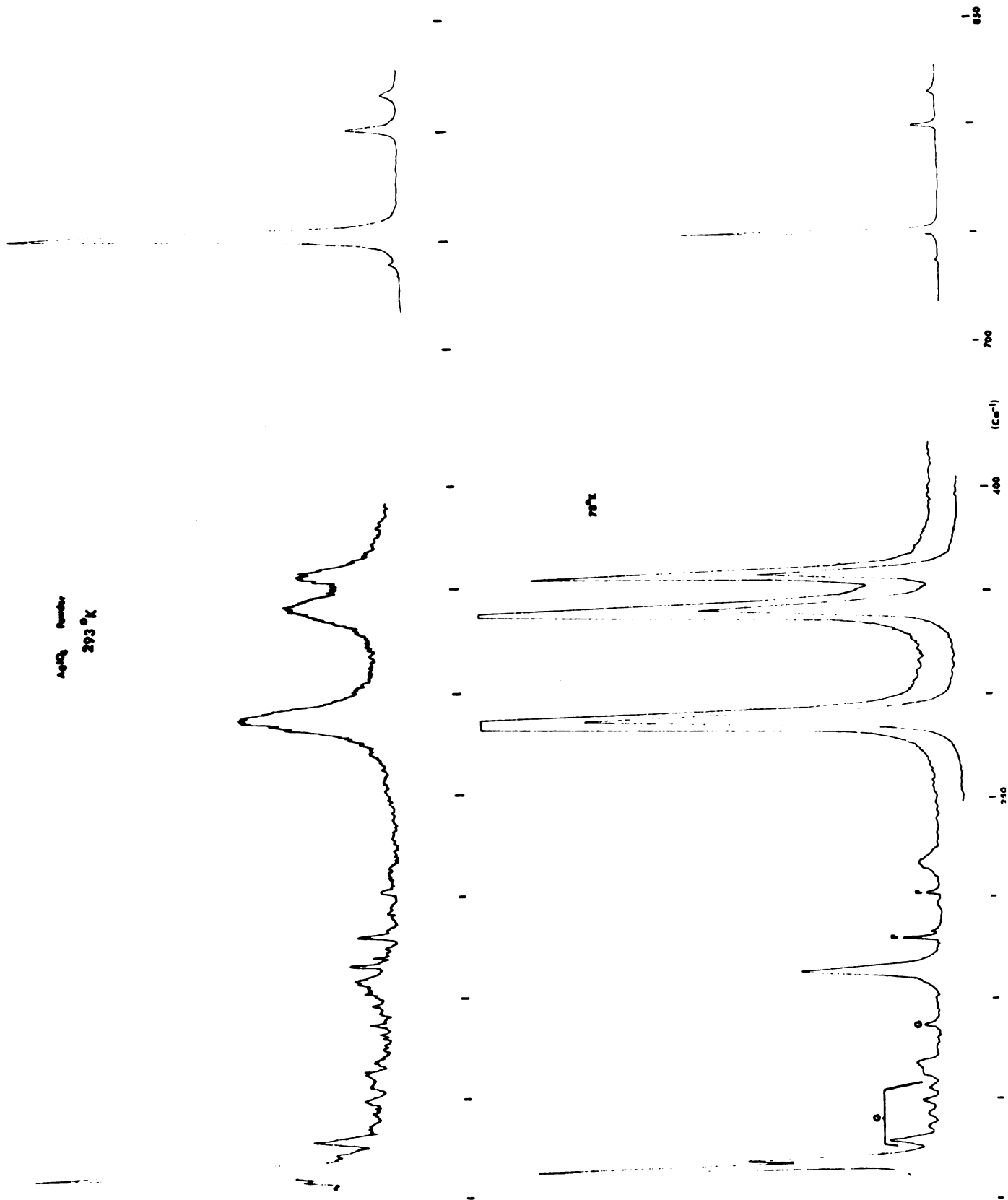


Figure 21

Raman spectrum of NH_4IO_4 powder at 293° and 81°K.

Figure 22

Raman spectrum of NH_4^+ fundamentals of NH_4IO_4 powder at 293° and 90°K.

Table X

Lattice modes of periodate crystals at $T \approx 293^\circ\text{K}$ (cm^{-1})

Symmetry	Na^+	K^+	Rb^+	Ag^+	NH_4^+
B_g	95.5	69.6	54.0	65.1	63.6
E_g	107.4	87.6	68.7	----	82.7
A_u^a	126.	98.	---	---	88.
E_g	147.3	116.4	84.6	---	129.0
A_g^b	162.8	132.8	113.9	159.1(?)	201.8
E_u^a	162	140.	76.	86.	190.
E_g	210.7	----	148.9(?)	---	---

a. Infrared active (u subscripted) modes from ref. 39.

b. Incorrectly assigned as E_g in ref. 39.(?) Implies symmetry assignment by analogy from NaIO_4 is speculative.

Table XI

Raman active lattice modes of periodate crystals near liquid N₂ temperature (in cm⁻¹).

Symmetry	T(°K) 81°	97°	80°	80°	81°
	Na ⁺	K ⁺	Rb ⁺	Ag ⁺	NH ₄ ⁺
B _g	97.7	72.2	55.5	68.6	64.8
E _g	111.2	93.2	73.9	71.3(?) 113.7(?)	89.5
E _g	153.1	122.0	90.0	118.2	140.6(?)
A _g	169.4	145.4	128.3	164.8	148.6(?) 195.3(?)
E _g	218.3	178.8	153.2(?)	217.9	216.2(?) 240.7(?)

(?) Implies symmetry assignment by analogy from NaIO₄ is speculative.

Table XII

Fundamental vibrations of solid periodates at $T \approx 293^\circ\text{K}$ (cm^{-1})^a

Fundamental	Symmetry	Na ⁺	K ⁺	Rb ⁺	Ag ⁺	NH ₄ ⁺
ν_1	A _g	784.2	795.6	797.0	753.1	796.5
ν_1	O ¹⁸ (Raman)	768.2	779.3	779.1	739.1	779.6
ν_1	B _u ^b	791	796	793	795	792
ν_2	A _g	290.2	278.0	273.8	288.7 ^c	277.3
ν_2	B _g	300.4	292.7	286.7		290.5 ^e
ν_2	A _u	264	264	268	250	262
ν_3	E _g	831.7	844.1	845.7	800.5	842.2
ν_3	B _g	847.3	856.9	853.3	814.3	851.7
ν_3	E _u	850	881	848 ^c	848	845
ν_3	A _u	831	870		863	862
ν_3	O ¹⁸ (Raman)					826.5
ν_4	E _g	356.6	336.6	326.9	342.4	290.5(?) ^e
ν_4	B _g	374.1	346.4	336.4	357.9	337.3
ν_4	E _u	368	398	398	394	398
ν_4	A _u	322	338	370	346	372
			314	306	308	316

a. Infrared active modes from ref. 39.

b. B_u is inactive, but $\nu_1\text{B}_u$ is still seen weakly in I.R. (ref. 39).

c. Second component expected in this region apparently not resolved.

d. Apparently one E_u lattice mode also mixes with ν_4 . The assignments were not distinguished in ref. 39.

e. Resolved only at low temperatures.

Table XIII

Raman active fundamentals of solid periodates near liquid nitrogen temperature (in cm^{-1}).

T(°K)		81°	97°	80°	80°	81°
Fundamental	Symmetry	Na ⁺	K ⁺	Rb ⁺	Ag ⁺	NH ₄ ⁺
ν_1	A _g	783.9	797.5	798.3	754.0	796.3
ν_1	O ¹⁸	768.4	780.2	780.0	739.8	777.9
ν_2	A _g	292.0	278.0	274.2	289.9 ^a	259.7
ν_2	B _g	301.5	295.1	287.8		285.7 ^b
ν_3	E _g	832.3	845.9	847.1	801.7	841.7
ν_3	B _g	848.2	858.3	858.1	817.4	849.0
ν_3	O ¹⁸			829.4	783.7	
ν_4	E _g	358.6	337.7	328.0	342.9	298.0 ^b
ν_4	B _g	377.0	349.3	338.4	360.1	339.1

a. Second component of ν_2 apparently not resolved.

b. These two bands are not resolved at room temperature and are assigned only by relative position.

in aqueous solution⁴⁸ at 780, 793 and 826 cm^{-1} . Two similar small peaks were observed in the AgIO_4 spectra (Figure 20) and are again best assigned as impurity bands. Also, in the AgIO_4 spectrum the second Raman-active component of ν_2 was not resolved, even at low temperatures, and it is possible that the sixth lattice mode (B_g) may have been observed as a shoulder on the E_g (118.2 cm^{-1}) band, but this peak is more probably a grating ghost. The lower quality of the AgIO_4 spectra results from the fact that the powder sample was yellow, and even the $\text{Kr}^+ 5682 \text{ \AA}$ laser line burned the sample, so the spectra were recorded using the weaker $\text{HeNe } 6328 \text{ \AA}$ laser line.

The NH_4IO_4 spectra are not expected to be completely analogous to the spectra of the other periodates, since the ammonium ion would be expected to have librational degrees of freedom (an E_g and an A_g mode being Raman active), and there are in addition the same internal vibrational degrees of freedom for the NH_4^+ ion as in the IO_4^- ion. Since the NH_4^+ is also on an S_4 site, the group theoretical predictions for the NH_4^+ vibrations are completely equivalent to the correlation diagram (Table VII) for IO_4^- . The lattice region (at 81°K) shows two additional high frequency peaks. However, since the assignment can no longer be made in analogy with the NaIO_4 single crystal data, we cannot assign the symmetries in this region of the NH_4IO_4 spectra. Also, the bending (ν_2 and ν_4) region of the IO_4^- of NH_4IO_4 shows only three components at room temperature, although upon cooling the expected fourth component becomes resolved.

The NH_4^+ fundamental regions are shown in Figure 22 with the peak frequencies listed in Table XIV. Also observable on this spectrum (Figure 22) is a weak, broad peak at $\sim 1709 \text{ cm}^{-1}$ which is either $2\nu_3$ of IO_4^- or an impurity, and a small structureless peak at $\sim 2833 \text{ cm}^{-1}$ that shows multiplet structure at 91°K , which is assigned as an impurity. The other sharp features (on the sides of the high gain scan of ν_1 and ν_3 at 293°K and one on either side of the 91°K scan of ν_1 and ν_3) are laser fluorescence lines that were not filtered in order to obtain maximum intensity.

Interpretation of Intermolecular Forces

With this data we will attempt to interpret the shifts in frequency of the internal modes of the IO_4^- ion in the various crystals in terms of the intermolecular potentials described earlier, and to assign the external lattice modes to principally one symmetry coordinate whenever possible.

The lattice constants^{25,45} and cation electronegativities⁴⁹ for the periodates of interest are listed in Table XV. As noted earlier, there are various methods of interpreting the intermolecular forces in the Scheelite crystals. Because of the large number of possible graphs that could be drawn to test the various models, only least squares fits to the majority of the plots will be included, with only the graphs of plots specifically discussed included.

Table XVI lists the appropriate values for the distances of the first three nearest neighbor anions and cations for each of the periodates. From Figure 12 it can be determined that the first

Table XIV

Fundamental frequencies of the NH_4^+ group in solid NH_4IO_4 (cm^{-1}).

Literature frequency ^a			Raman active factor group components	293°K Frequency	91°K Frequency
3033	ν_1	A_1	A_g	3170.6	3146.5
1685	ν_2	E	A_g	1679.8	1649.0
			B_g		1656.6
3134	ν_3	T_2	E_g	3236.5	3206.9
			B_g		
1397	ν_4	T_2	E_g	1429.4	1433.8
			B_g		1449.9

a. From reference 24.

Table XV

Unit cell dimensions^a and cation electronegativities^b of periodate crystals with the Scheelite structure.

Compound	a_o (Å)	c_o (Å)	Cation Electronegativity
NaIO ₄	5.32	11.93	1.01
KIO ₄	5.75	12.63	0.91
RbIO ₄	5.921	13.052	0.89
AgIO ₄	5.374	12.094	1.42
NH ₄ IO ₄	5.938	12.790	----

a. References 38 and 42.

b. Reference 43.

Table XVI

Distances of first three sets of nearest neighbors (anions and cations)
for the periodates of Scheelite structure (in Å).

Crystal	nearest neighbor $M^+IO_4^-(4)^a$	2nd nearest (4)	3rd nearest (2)
$NaIO_4$	3.76	4.99	5.96
KIO_4	4.07	5.31	6.32
$RbIO_4$	4.19	5.48	6.53
$AgIO_4$	3.80	5.05	6.05
NH_4IO_4	4.20	5.41	6.40

Crystal	nearest neighbor $IO_4^-IO_4^-(4)$	2nd nearest (4)	3rd nearest (4)
$NaIO_4$	4.00	5.32	7.52
KIO_4	4.27	5.75	8.13
$RbIO_4$	4.41	5.92	8.37
$AgIO_4$	4.04	5.37	7.60
NH_4IO_4	4.36	5.94	8.40

a. Number in parentheses indicates the number of symmetrically
equivalent neighbors at this distance.

three nearest neighbor anion-cation distances are $\frac{\sqrt{2}}{2} a$, $(\frac{1}{4} a^2 + \frac{1}{8} c^2)^{1/2}$ and $\frac{1}{2} c$ respectively, and that the first three anion-cation distances are $[(\frac{1}{2}a)^2 + (\frac{1}{4}c)^2]^{1/2}$, a , and $\sqrt{2} a$ respectively. From Table XVI it is clear that the assumption that nearest neighbor interaction is the only one of significance (in either model) is a poor approximation. However, since the electronegativity of the IO_4^- group is not known, the next nearest neighbor (another anion) cannot be included in the ionic (Ulbricht and Kriegsmann) model,²⁷ while in Scott's model²⁶ it would appear to be incorrect to include the anions at a distance of $a \text{ \AA}$, while at the same time ignoring a cation at $\frac{\sqrt{2}}{2} a \text{ \AA}$ away. Thus the calculations were performed using only nearest neighbor distances.

Table XVII lists the linear least squares fits^{50,51} for $\nu_1 (A_g)$ and the two Raman-active components of $\nu_3 (B_g \text{ and } E_g)$ for the plots of frequency and frequency squared versus the zeroth, first and second derivatives of the two potential functions. The two potential function forms used were $V(r) \propto \frac{e}{r}$ for the ionic model, where e is the cationic electronegativity and r the cation-anion nearest neighbor distance from Table XVI, and $V(R) \propto \frac{1}{R^6}$ for the van der Waals' model where R is the anion-anion nearest neighbor distance from Table XVI.

It is clear from Table XVII that there is more accuracy (nearly an order of magnitude) in the ionic model, since the uncertainty in frequency (y variance) is much greater in the plots for the van der Waals' (anion-anion interaction) model. That is, the dominant factor

Table XVII

Parameters in linear least squares fits of ν_1 (A_g) and ν_3 (E_g and B_g) for periodate crystals of the Scheelite structure.

e = electronegativity (cation); r = $r_{\text{cation-anion}}$; R = $r_{\text{anion-anion}}$					
y = mx+b					
y	x	m	b	y variance	$\sqrt{b}$
ν_1	er^{-1}	-2.771×10^2	857.2	1.4	
ν_1	er^{-2}	-9.357×10^2	846.9	3.6	
ν_1	er^{-3}	-3.191×10^3	838.7	5.3	
ν_1	R^{-6}	-2.736×10^5	835.5	18.0	
ν_1	R^{-7}	-9.763×10^5	828.2	18.1	
ν_1	R^{-8}	-3.552×10^6	822.8	18.1	
$(\nu_1)^2$	er^{-1}	-4.295×10^5	7.284×10^5	2.025×10^3	853.5
$(\nu_1)^2$	er^{-2}	-1.451×10^6	7.125×10^5	5.374×10^3	844.1
$(\nu_1)^2$	er^{-3}	-4.948×10^6	6.998×10^5	7.945×10^3	836.5
$(\nu_1)^2$	R^{-6}	-4.264×10^8	6.952×10^5	2.773×10^4	833.8
$(\nu_1)^2$	R^{-7}	-1.522×10^9	6.839×10^5	2.780×10^4	827.0
$(\nu_1)^2$	R^{-8}	-5.537×10^9	6.754×10^5	2.787×10^4	821.8
$\nu_3 E_g$	er^{-1}	-2.849×10^2	907.3	1.1	
$\nu_3 E_g$	er^{-2}	-9.634×10^2	896.8	3.3	
$\nu_3 E_g$	er^{-3}	-3.289×10^3	888.5	5.0	
$\nu_3 E_g$	R^{-6}	-2.863×10^5	886.0	18.2	
$\nu_3 E_g$	R^{-7}	-1.022×10^6	878.4	18.2	
$\nu_3 E_g$	R^{-8}	-3.718×10^6	872.7	18.3	
$(\nu_3 E_g)^2$	er^{-1}	-4.688×10^5	8.165×10^5	1.563×10^3	903.6
$(\nu_3 E_g)^2$	er^{-2}	-1.586×10^6	7.993×10^5	5.104×10^3	894.0
$(\nu_3 E_g)^2$	er^{-3}	-5.417×10^6	7.855×10^5	7.906×10^3	886.3
$(\nu_3 E_g)^2$	R^{-6}	-4.738×10^8	7.819×10^5	2.970×10^4	884.3
$(\nu_3 E_g)^2$	R^{-7}	-1.691×10^9	7.693×10^5	2.977×10^5	877.1
$(\nu_3 E_g)^2$	R^{-8}	-6.153×10^9	7.599×10^5	2.985×10^5	871.7

Table XVII (continued)

$\nu_3 B_g$	er^{-1}	-2.604×10^2	913.1	4.6	
$\nu_3 B_g$	er^{-2}	-8.697×10^2	902.9	6.5	
$\nu_3 B_g$	er^{-3}	-2.942×10^3	894.8	8.0	
$\nu_3 B_g$	R^{-6}	-2.267×10^5	886.9	19.1	
$\nu_3 B_g$	R^{-7}	-8.094×10^5	880.9	19.1	
$\nu_3 B_g$	R^{-8}	-2.946×10^6	876.4	19.1	
$(\nu_3 B_g)^2$	er^{-1}	-4.346×10^5	8.280×10^5	7.695×10^3	909.9
$(\nu_3 B_g)^2$	er^{-2}	-1.452×10^6	8.109×10^5	1.079×10^4	900.5
$(\nu_3 B_g)^2$	er^{-3}	-4.914×10^6	7.975×10^5	1.318×10^4	893.0
$(\nu_3 B_g)^2$	R^{-6}	-3.799×10^8	7.845×10^5	3.179×10^4	885.7
$(\nu_3 B_g)^2$	R^{-7}	-1.356×10^9	7.744×10^5	3.182×10^4	880.0
$(\nu_3 B_g)^2$	R^{-8}	-4.937×10^9	7.669×10^5	3.187×10^4	875.7

controlling the shift in internal stretching frequencies in the periodate crystals is the electrostatic site interaction rather than the factor group resonance coupling. Similar results, but with the opposite trend in frequencies occurred for the bending (ν_2 and ν_4) modes. It should also be noted that in all cases, the y variance increases with the higher derivatives of the potential function (the straight line is less accurately followed) while the intercepts (which should give the frequency at $r = \infty$, i.e. isolated) show exactly the opposite effect, approaching more and more closely the solution frequencies with the higher order derivatives of the potential function. However, since the gaseous (truly isolated) vibrational frequencies are not available, the error in intercept is most likely due to solvent effects. Also, in the ionic model, where the nearest neighbor cations lie in the xy plane and the B_g motions involve motion along the unique (z) axis there is noticeably less accuracy in the least squares plots, while for the van der Waals' model, where the nearest neighbor anions are not in the xy plane, the B_g modes are approximately the same in accuracy (y variance approximately the same).

Figures 23 and 24 show plots of ν_1 versus er^{-1} and ν_1 versus R^{-6} respectively. The plots of ν_1 are given instead of $(\nu_1)^2$ since the percent variance of the square of the frequency is slightly larger than that of the first power of the frequency. It is clear from Figures 23 and 24 that the important difference in the two models comes from the inclusion of the electronegativity of the cation. This is not very noticeable for Na^+ , K^+ and Rb^+ where there is just a small

Figure 23

Plot of frequency $\nu_1(A_g)$ versus electronegativity/ $r_{\text{anion-cation}}$.

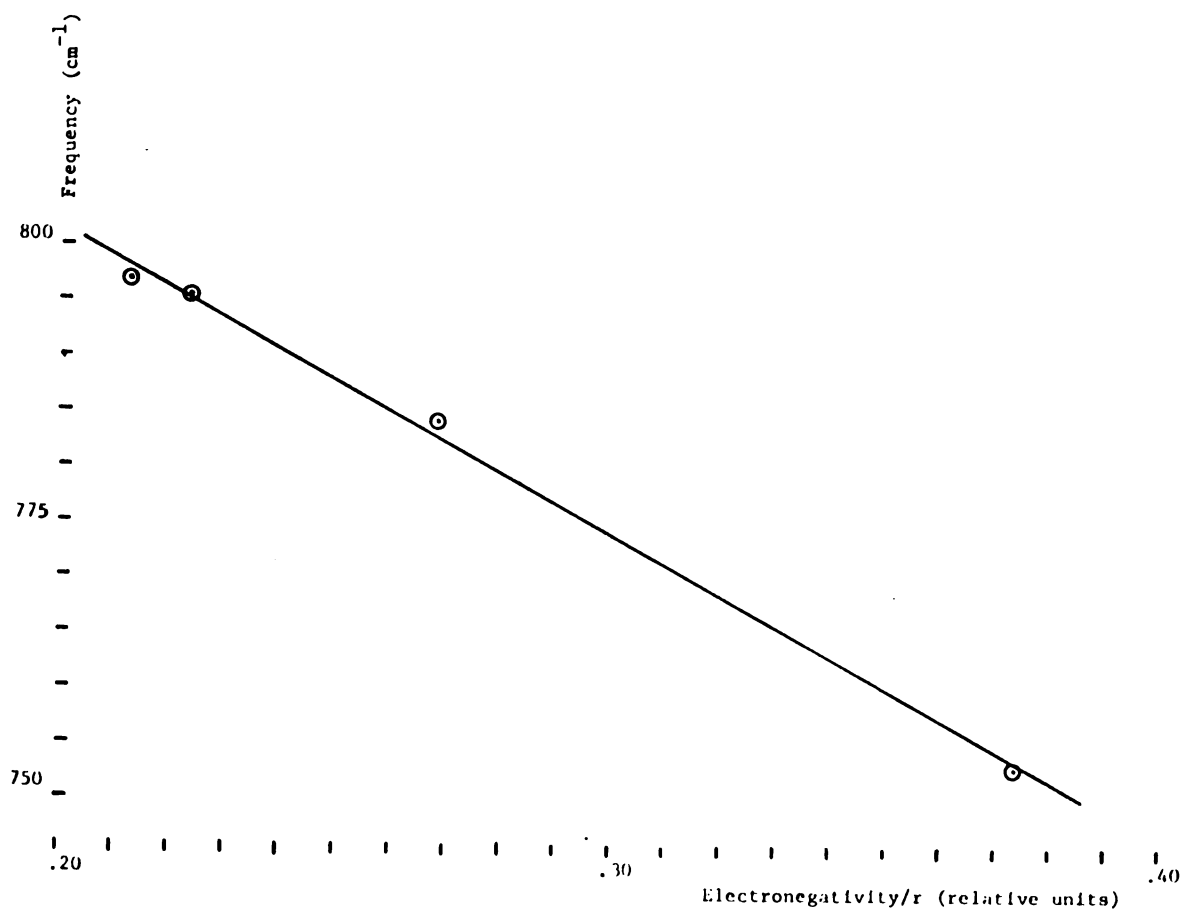
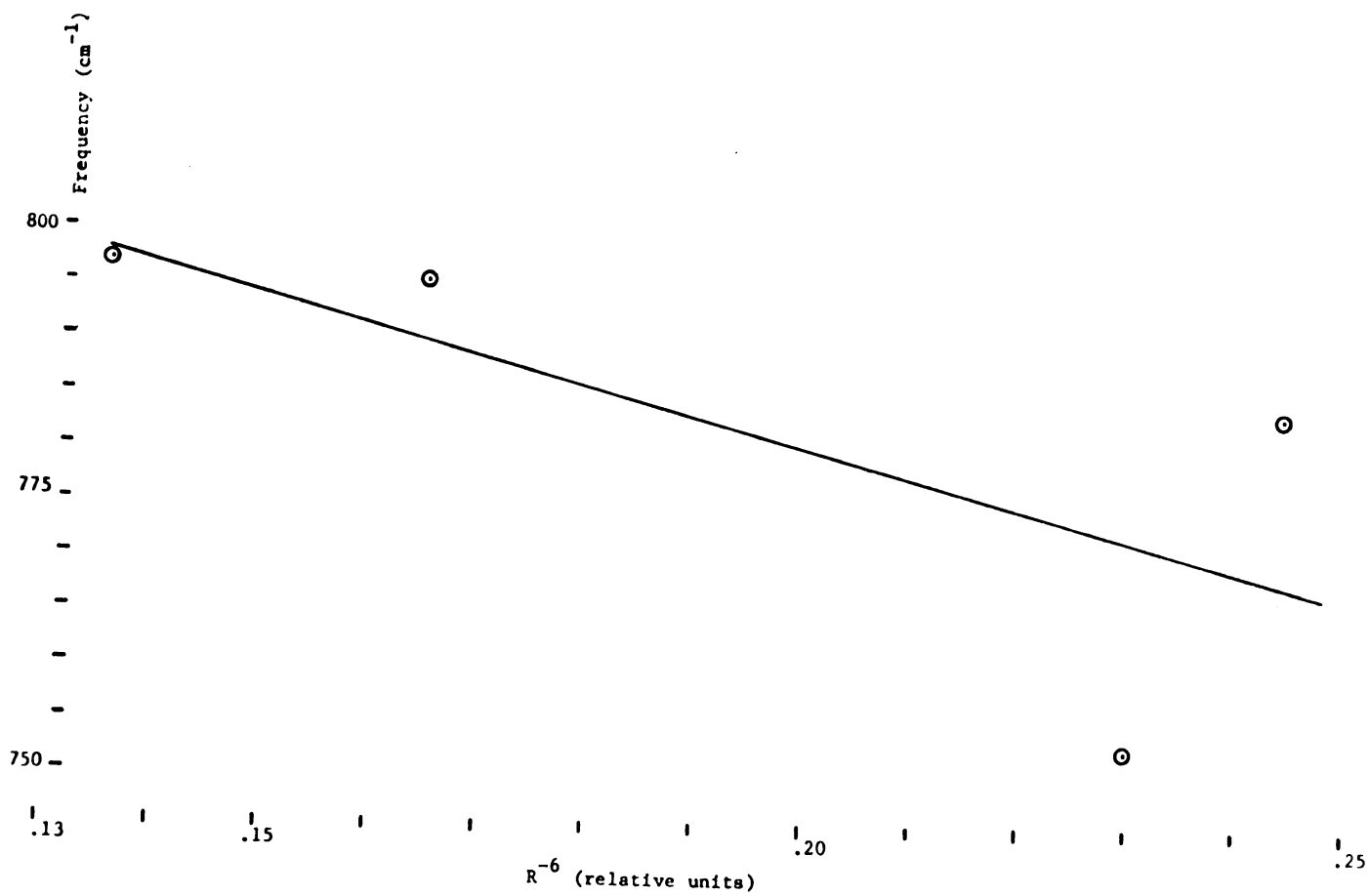


Figure 24

Plot of frequency $\nu_1(A_g)$ versus $R_{\text{cation-anion}}^{-6}$.



change in electronegativity (see Table XV); however the Ag^+ ion makes the effect much clearer. The frequencies of the AgIO_4 modes appear to be much too low compared to the other periodate salts without inclusion of the significantly higher electronegativity of silver. Thus, the most important factor in determining the shifts in the frequencies of an internal mode in these crystals appears to be the strength of the ionic interaction between cations and anions. As the ionic character increases, the stretching frequencies shift to higher values, or conversely, as the covalency increases in the crystals, the internal anionic stretching frequencies decrease. The changes in the accuracy of the plots as a function of potential derivatives (and frequency or frequency squared) are small enough so that although the best fit results from plotting frequency versus potential function in all cases, it would be unreasonable to exclude the validity of the other plots on the basis of our data alone. Considerably more experimental data or rather extensive theoretical calculations would be necessary to conclude which plots are rigorously correct.

The Raman-active lattice modes of the periodates (Table X and XI) can only be approximately assigned to particular symmetry coordinates within a given symmetry block. However the similarity in frequency shifts between the various crystals for the highest frequency E_g lattice mode and the $A_g(R_z)$ periodate libration leads us to conclude that this is the E_g mode principally of librational character. It should be noted that even the frequency of the A_g

librational mode (purely a motion of the periodate ion) varied considerably through the series of crystals.

The translations of the cations and anions appear to be mixed, but not just to the extent of being dependent on the reduced mass of the cation-anion pair. No linear plot was obtained for the E_g lattice modes [plotting frequency and frequency squared versus a. $1/\mu$ (μ = the cation-anion reduced mass), b. $1/\sqrt{\mu}$, c. a^2 (a = the xy lattice constant), d. $a^2/\sqrt{\mu}$, e. ea^2/μ (e = the cation electronegativity), f. $ea^2/\sqrt{\mu}$, g. $1/\sqrt{m}$ (m = the cation mass), h. a^2/m , i. $ea^2/\sqrt{m}$], and thus we cannot confirm the above assignment of the librational E_g mode as being the one of highest frequency. It is important to note that the silver periodate lattice modes were the furthest from any of the linear plots, implying that again the greatest shortcoming of our attempts at obtaining a correlation of the frequencies in the different crystals is our inability to properly compensate for the change in ionic character of the crystals.

Although this outline of the assignment for the lattice modes is extremely qualitative, it is felt that further assignment would be too speculative without a detailed normal coordinate analysis calculation, which requires many unknown force constants, and is thus unfeasible at the present time.

The ammonium fundamentals (much weaker than the periodates in the Raman spectrum) were observed (at 81°K) to show splitting on two (ν_2 and ν_4) of the three expected to be split on the basis of

the correlation diagram. At room temperature all of the NH_4^+ fundamentals were much too broad to show similar splittings. Since these splittings are predicted to occur at the site (even before factor group coupling is considered), we can conclude from this only that the NH_4^+ does not rotate freely. In addition to this, two additional high-frequency lattice modes (the number predicted for NH_4^+ librations), which were not observed in any of the other periodate crystals, are most probably the NH_4^+ librations. However, these also were not observed at room temperature.

Conclusions

All of the Raman-active fundamentals of the periodate crystals of the Scheelite structure have been identified and assigned symmetries with the exception of one component of ν_2 in AgIO_4 . We find the potential form that appears to dominate in determining the frequency shifts of the internal modes is of the ionic (site effect) form. This is in agreement with Ulbricht and Kriegsmann's analysis of the perrhenate spectra,²⁷ but does not agree with Scott's analysis of the tungstates.²⁶ However Scott did not study cations with greatly differing electronegativities. More recently, Kravitz³⁷ has reported that PbWO_4 also does not follow Scott's predictions, and this is expected since Pb has a considerably higher electronegativity than the cations Scott studied.

In NH_4IO_4 splittings on the NH_4^+ fundamentals and additional lattice modes imply the NH_4^+ ion does not rotate freely; however, these observations do not exclude some type of one-dimensional rotation.

The very wide half-widths of the NH_4^+ fundamentals (particularly at 298°K) are indicative of rather extensive motion of the NH_4^+ ion.

In the lattice region, all but one (B_g translational) mode was observed and assigned symmetry. However, there was no clear distinction between the librational and the translational motions of the same symmetry, and the observed normal modes are apparently mixtures of the two types of motions of the anion as well as translations of the cation. It is also probable that the low frequency (bending) internal modes of the periodate mix to an appreciable extent with the external modes.

Appendix III

APPENDIX III

Construction of a Correlation Diagram.

Although the group theoretical basis for the factor group analysis of crystals is accurately presented in references 22 and 23, and correlation diagrams are also listed in Molecular Vibrations by Wilson, Decius and Cross,⁵² it is rather difficult to draw directly from these references the insight into the factor group analysis. This appendix in no way replaces the above references, but rather is designed to present a simpler, more physically oriented explanation of the factor group analysis, and then to construct the factor group used in the analysis of the Scheelite structure.

NaIO_4 is of the Scheelite structure, which has the C_{4h}^6 space group with two molecules per primitive unit cell. Both the cations and anions are on sites of S_4 symmetry. These are the necessary x-ray data for the analysis. If this information is not available (as is often the case for molecular compounds and for hydrogen-containing compounds) then the limited data available are used in conjunction with all possible factor groups to generate the various possible spectral predictions, and under favorable circumstances the crystal symmetry may be inferred from the spectroscopic results.

After the degrees of freedom of the free molecule (or ion) have been assigned to their respective symmetry classes (including external translations T_x , T_y , and T_z and rotations R_x , R_y , and R_z) using the isolated molecular point group, one considers how these are affected by the crystallographic site.

The site group is a point group that is a subgroup of the crystal space group. It consists of all symmetry operations which leave the site invariant. Thus all site group operations are point operations and screw axes and glide planes cannot belong to a site group. Any point has some site group associated with it (at least C_1), and tabulation of types and numbers of equivalent sites are given in Halford's paper²² and the International Tables for X-ray Crystallography.⁵³ The effect of the site group on the molecular vibrations is to rename the irreducible representations of the molecular point group to correlate with irreducible representations of the site group. In the usual case that the site is of lower symmetry than the molecule, the site may lift degeneracies present in the molecular point group, creating closely spaced vibrational components from one isolated molecular vibration.

The final step in the analysis is the coupling of the site symmetry modes in the factor group. The factor group is defined as the crystallographic space group minus all pure translational operations. Thus the factor group is a finite subgroup of the space group and has the physical significance of having the symmetry of the primitive unit cell where one treats all translations that transform one unit cell into another translationally equivalent unit as being the identity operation. By using this rule, screw axes and glide planes will just become point operations (rotations and reflections) because the associated motion is just a translation. Thus the factor group is isomorphous with a point group. That is, if one looks

at a three dimensional picture of a unit cell, some of the point group operations of the factor group will not be present. However, corresponding space group operations will be present and the transformation properties of the two groups will be the same, so that one can predict the spectra from the point group isomorphous with the factor group.

In order to see how the irreducible representations of the site groups transform under the symmetry of the factor group one uses the equation:

$$b_K^{ir} = \sum_R \chi_K^\mu(R) \chi_i^r(R) / h^r$$

where b_K^{ir} is an integer denoting how many times the ith irreducible representation of the rth site group appears in the Kth irreducible representation of the factor group μ . The summation is over all symmetry elements (R) of the site group (note: site group = subgroup of the factor group, therefore all elements are also present in the factor group); $\chi_K^\mu(R)$ and $\chi_i^r(R)$ are the corresponding traces (i.e., elements of the corresponding character tables) and h^r is the order of the rth site group. Physically, this means that coupling the identical motions of the equivalent occupied sites in the unit cell will, in general, create a reducible representation of the factor group which can be decomposed by the equation above into the various irreducible representations of the factor group. Infrared or Raman activity is then obtained by observing which irreducible representations of the factor group transform as vectors (IR) or tensor components (Raman).

We shall now consider NaIO_4 and construct the Scheelite correlation diagram (Table VII). The IO_4^- group is tetrahedral in solution, and although this is not necessarily so in the crystal, the perturbation on the T_d symmetry will be assumed small enough that the internal modes of the anion group can be assigned symmetries under the T_d point group. The internal coordinates for a tetrahedron are depicted in Figure 13 along with their appropriate symmetries. One finds from any character table that the translations (T_x , T_y and T_z) of the tetrahedron form a basis for the T_1 irreducible representation and the rotations (R_x , R_y and R_z) a basis for T_2 . Therefore we see we have one internal mode (ν_1) of A_1 symmetry, one of E symmetry (ν_2), one external mode (translational) of T_1 symmetry, and 2 internal vibrations (ν_3 and ν_4) and one external (rotational) mode of T_2 symmetry. We shall now carry the $\nu_2(E)$ mode through in detail. The other symmetries may be treated in analogous fashion.

First from the character tables²⁴ for the molecular (ionic) point group (T_d) and site group S_4 we find:

T_d	E	$8C_3$	$3C_2$	$6S_4$ (or S_4^3)	$6\sigma_d$
$\vdots$					
E	2	-1	2	0	0
$\vdots$					
S_4	E	S_4	C_2	S_4^3	
A	1	1	1	1	
B	1	-1	1	-1	
E	$\begin{Bmatrix} 1 \\ 1 \end{Bmatrix}$	$\begin{Bmatrix} i \\ -i \end{Bmatrix}$	$\begin{Bmatrix} -1 \\ -1 \end{Bmatrix}$	$\begin{Bmatrix} -i \\ i \end{Bmatrix}$	
(Note: A+B	2	0	2	0)	

We see that to obtain the characters of the E irreducible representation of T_d symmetry we must add one each of the A and B irreducible representations of the S_4 group. The elements of the molecular group T_d that are not in the site group S_4 are ignored.

Now from the C_{4h} character table we find the b_K^{ir} . As an example we will calculate the $b_K^{AS_4}$'s. That is, to which (K) irreducible representations of the factor group C_{4h} does the A irreducible representation of the S_4 site go?

$$b_K^{AS_4} = \frac{1}{4} \sum_{R_1}^{R_4} \chi_K^{C_{4h}}(R_i) \chi_A^{S_4}(R_i) / 4 \quad \text{dimension of } S_4$$

elements of S_4

$$\begin{aligned} \therefore b_{A_g}^{AS_4} &= [\chi_{A_g}^{C_{4h}}(E) \chi_A^{S_4}(E) + \chi_{A_g}^{C_{4h}}(S_4) \chi_A^{S_4}(S_4) \\ &\quad + \chi_{A_g}^{C_{4h}}(C_2) \chi_A^{S_4}(C_2) + \chi_{A_g}^{C_{4h}}(S_4^3) \chi_A^{S_4}(S_4^3)] / 4 \\ &= 1 \end{aligned}$$

similarly: $b_{B_u}^{AS_4} = 1$ and $b_{E_g}^{AS_4} = b_{A_u}^{AS_4} = b_{B_g}^{AS_4} = b_{E_u}^{AS_4} = 0$.

Thus we see that $\nu_2(E)$ of the T_d IO_4^- ion has its two-fold degeneracy lifted at the site, creating one A and one B symmetry mode under the S_4 site. Furthermore, the A mode of the S_4 site is coupled with the A mode of the other molecule in the primitive unit cell to form one mode of A_g and one of B_u symmetry in the factor group C_{4h} .

A similar procedure for all other symmetries leads to the Table VII.

Tables (with occasional errors) of these correlation diagrams are listed in references 22 and 52; however it is convenient to be able to reconstruct ~~these~~ data for the cases of interest to insure accuracy.

RAMAN SPECTRA OF PURE AND MIXED CRYSTALS OF ACETYLENE AND DEUTERATED
ACETYLENE

Introduction

The vibrational spectrum of solid acetylene has been of interest for a number of years.⁵⁴⁻⁵⁸ X-ray crystallographic studies^{59,60} have yielded the space group T_h^6 with four molecules per primitive unit cell on S_6 sites for the higher temperature (β) phase (analogous to CO_2). However, cooling through the phase transition ($133^\circ K$ for C_2H_2)⁵⁹ shatters single crystals, and the resulting X-ray powder data have been able to determine only that an orthorhombic structure is formed.⁵⁶

Through previous spectroscopic studies,⁵⁴⁻⁵⁸ it has been proposed that the lower temperature (α) phase has space group D_{2h}^{18} (analogous to the halogens), with two molecules per primitive unit cell on C_{2h} sites (with the C_2 axis of the site perpendicular to the molecular axis).

This study was initiated to provide a complete, temperature dependent study of the Raman spectra of the crystalline phases of acetylene to confirm the crystal structure predictions and provide data on intermolecular forces in these crystals. Both phases of C_2H_2 and C_2D_2 were studied as a function of temperature and in the lower temperature phase, mixed crystals (from 1.5 to 5% of one isotope doped into the other) were studied.

Interpretation

The correlation tables for the two phases of acetylene are drawn in Table XVIII. (See Appendix III for method of construction.)

From Table XVIII, we see that for the lower temperature phase, the two Σ_g^+ vibrations (ν_1 and ν_2) of C_2H_2 are coupled in the factor group (Davydov split) into an A_g and B_{3g} mode; and the $\Pi_g(\nu_4)$ bending mode is site split (into A_g and B_g modes) and then each of these modes is factor group coupled giving four nondegenerate unit cell modes (A_g , B_{1g} , B_{2g} and B_{3g}). The lattice librations would similarly give rise to four one-dimensional modes, while the translations and the other internal vibrations (ν_3 and ν_5) are infrared and not Raman active. The higher temperature (β) phase Raman spectrum would be expected to have two components (A_g and T_g) for the symmetric stretching vibrations (ν_1 and ν_2) and three ($2T_g$ and E_g) for the Π_g bend and also for the lattice librations. The lattice translations and ν_3 and ν_5 would again be infrared and not Raman active.

Following Dow's development³⁵ we see that the isolated frequencies are affected by two interaction terms in the crystal:

$$D = \sum_r \int \{ |\phi'_p \phi_r|^2 - |\phi_p \phi_r|^2 \} V_{pr} d\tau$$

$$M^\alpha = T \sum_r B_{\alpha a}^* B_{\alpha b} \int (\phi'_p \phi_r)^* V_{pr} (\phi_p \phi'_r) d\tau$$

where the ϕ_i represent the vibrational states of the isolated molecule (a prime (') indicates that molecule is vibrationally excited), V_{pr}

Table XVIII

Correlation diagram for the lower temperature (α) phase of crystalline C_2H_2 .

Molecular point group $D_{\infty h}$	Site group $C_{2h}(\perp)$	Factor group D_{2h}	Activity
ν_1, ν_2 Σ_g^+	A_g	A_g	x^2, y^2, z^2
		B_{3g}	yz
$\nu_4, (R_x, R_y)$ Π_g	B_g	B_{1g}	xy
		B_{2g}	xz
ν_3, T_z Σ_u^+	B_u	B_{1u}	z
		B_{2u}	y
$\nu_5, (T_x, T_y)$ Π_u	A_u	A_u	inactive
		B_{3u}	x

Correlation diagram for the higher temperature (β) phase of crystalline C_2H_2 .

Molecular point group $D_{\infty h}$	Site group S_6	Factor group T_h	Activity
ν_1, ν_2 Σ_g^+	A_g	A_g	x^2, y^2, z^2
		T_g	(xy, yz, zx)
$\nu_4, (R_x, R_y)$ Π_g	E_g	E_g	$(x^2+y^2-z^2, x^2-y^2)$
$\nu_3, (T_z)$ Σ_u^+	A_u	A_u	
		T_u	(x, y, z)
$\nu_5, (T_x, T_y)$ Π_u	E_u	E_u	

is an interaction (perturbation) potential assumed to be the sum of pairwise molecule interactions, the B matrix is the unitary matrix that converts from internal (unperturbed molecular normal coordinates) to symmetry (factor group) coordinates, and T counts the number of equivalent sites the molecules occupy per primitive unit cell. The summations are over all molecules (r) other than p. The D term, analogous to a valence bond coulomb integral, is the (site) effect of the static crystal field. The M term, analogous to a valence bond exchange integral, results from the exchange of energy between two molecules (p and r) in the crystal. If the two molecules (p and r) are translationally equivalent, M gives rise to a shift in the frequency of the fundamental, while if p and r are translationally inequivalent the M term will give rise to (factor group or Davydov) splitting of the fundamental. Thus, in the pure crystal, the isolated molecule's frequencies are shifted by the D term (site effect) and then both shifted and split by factor group (M term) coupling.

Isotopically substituted material which has significantly different vibrational frequencies (as is the case for substitution of deuterium for hydrogen) will exhibit the same total effect on the fundamentals of the pure crystal. In addition, by taking spectra of dilute mixtures of one of the isotopes mixed in the other, we can separate the D and M terms. If we assume the crystal structures and interaction potentials are the same, the D (site) term will remain the same regardless of whether the molecule is isolated in an isotopically

different crystal or if the surrounding molecules are the same isotope. However, if the surrounding molecules are isotopically different (to the extent that the vibrational modes are not nearly the same frequency) the M term will not exist, since the one vibrating molecule can no longer exchange its vibrational energy directly with a neighboring molecule. If we also assume harmonic coupling, the splitting due to the M term will be symmetric, therefore the shift of the isolated peak from the center of the pure crystal peaks will give a measure of the part of the M term that gives rise to a shift in frequency. Thus, the shift from the gaseous frequency to the isolated crystalline frequency gives a measure of the site (D) effect. Then the pure crystal spectra show the magnitude of M; the splitting giving M due to translationally inequivalent molecules, and the difference of the mean frequency of the split components from the isolated (mixed crystal) frequency measures M due to translationally equivalent molecules.

The relative intensities of the vibrational modes can be calculated by use of the "oriented gas" model based on the assumption of no molecular interactions.⁶¹ What needs to be done is take the Raman absolute intensity and depolarization ratio measurements of the gaseous molecule⁶² and determine from these the mean value ($\bar{\alpha}'$) and anisotropy (γ') of the polarizability derivative matrix for each internal vibration. It is then assumed that these quantities are not changed upon crystallization. For the librational lattice modes, one uses the molecular polarizability anisotropy measured by Bridge and Buckingham⁶³ and again assumes no change in this value and the moment of inertia upon crystallization for the calculation of the intensities.

For the two Σ_g^+ symmetric stretching modes of C_2H_2 (ν_1 and ν_2) there is the additional consequence of the change in composition of the normal modes upon deuteration. The "C-H" stretching (ν_1) normal mode has much less C $\equiv$ C bond stretching force constant involved in it than the corresponding "C-D" ν_1 stretch of C_2D_2 . Since a unit stretch of the C $\equiv$ C triple bond has associated with it a much larger polarizability change than the C-H bond, this additional mixing of the two Σ_g^+ symmetry modes must be considered before comparing the relative intensities of ν_1 to ν_2 in the two different isotopic species. To do this, the gas phase bond polarizabilities⁶² are multiplied by the coefficients of the eigenvectors of the normal coordinates obtained by a conventional "normal coordinate" analysis.⁶⁴ We will try to interpret the acetylene spectra by use of these models.

Experimental

C_2H_2 was obtained from the Matheson Co. and purified by repeated trap to trap (77°K to 193°K) vacuum distillation. The C_2D_2 (99.5%D) was obtained from the Stohler Isotope Chemical Corp. and was used without further purification. However, the vacuum manifold used for handling the sample was first treated with D_2O . The laser-Raman spectrometer was again the same as previously described (see the chapter on I_2 fluorescence-Experimental section). Three sampling techniques were used. For the higher temperature phase, a closed cell cooled by cold N_2 gas flow was used. The same dewar drawn in Figure 14 was fitted with a small sample tube passing through the cork stoppers and fitted with a stopcock for connection to a vacuum line. For the colder spectra (77°K to 30°K) a Malaker Corp. Cryomite Mark VII-C

was closed cycle helium refrigerator/fitted first with a spray-on sample head (Figure 25A) and later (for all data shown) with a closed sample head (Figure 25B). The closed cell design was developed so that the sample could be slowly annealed from above the phase transition down to $\sim 30^\circ\text{K}$. As soon as the spray-on style head was allowed to warm up to $\sim 100^\circ\text{K}$ the C_2H_2 sublimed away from the end surface of the copper block back to the colder portions of the cell and away from the useful sample area. In the smaller closed cell, a larger sample was sublimed into the head (~ 1 c.c.) until the sample inlet sidearm was sealed off with the sample. In this way, the annealing process could be carried out with only a relatively small loss of sample. The annealing noticeably reduced linewidths so that at 30°K all fundamentals were only $\sim 1\text{ cm}^{-1}$ (the inherent laser exciting line width) wide.

Results and Discussion

The Raman spectrum of the low-temperature (α) phase of crystalline C_2H_2 is shown in Figure 26 and the frequencies and relative intensities are listed in Table XIX. The spectrum (Figure 26) consists of three lattice bands (4 are expected on the basis of the correlation diagram, Table XVIII), three components of ν_4 (4 expected), three bands in the ν_2 region (two are expected; the small, low frequency band is due to C^{13}), and three bands in the ν_1 region (two expected, the weak one again being C^{13}). Figure 27 shows the corresponding C_2D_2 spectrum. There are two small grating ghosts ($\sim 49\text{ cm}^{-1}$ and 58 cm^{-1} respectively) and again 3 lattice modes, 3 components of ν_2 and 3 components of ν_1 with the two factor group split components barely resolved. The ν_4 band

Figure 25A

Spray-on cell for Malaker refrigerator.^a

Figure 25B

Closed sample head for Malaker refrigerator.^a

- a. Both sample cells were contained inside a 2-inch outer vacuum jacket.
- b. Attached to Malaker cold head.
- c. 1" Kovar seal.
- d. Spray-on nozzle.
- e. Remainder same as design B.
- f. Silver soldered.
- g. 1/2" Kovar seal.
- h. 1/8" Kovar seal.
- i. 1/16" thin-walled stainless steel tubing coil.
- j. 1/2" outside vacuum jacket spacer with 1/16" tubing feed-thru.

Figure 26

Raman spectrum of α C₂H₂ (30°K).

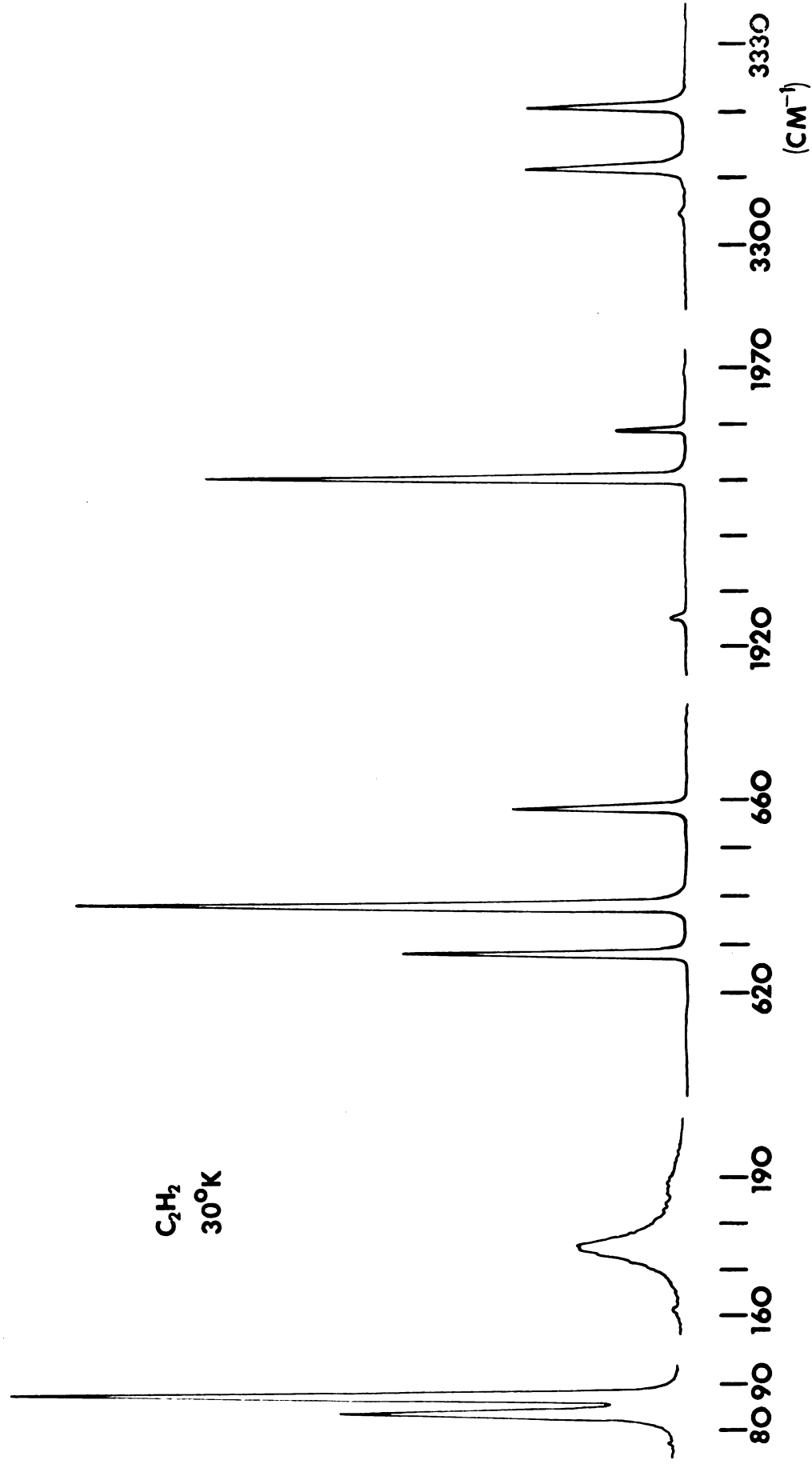


Table XIX

Frequencies and intensities of α -C₂H₂ and α -C₂D₂ at 30°K.

Assignment	C ₂ H ₂			C ₂ D ₂		
	Frequency (cm ⁻¹)	Width at 1/2 height ^b (cm ⁻¹)	Intensity ^a	Frequency	Width at 1/2 height ^b	Intensity
Lattice	83.6	2.0	43.5	71.1	3.0	43.7
	87.4	1.5	56.5	74.1	2.0	56.3
	174.9	5.5	8.7	152.1	6.0	15.5
ν_1	3311.5	1.0	6.2	2671.0 ^c	1.5	4.6
	3320.6	1.0	5.8			
ν_2 (C ¹³)	1925.3	1.0	0.8	1724.6	1.0	1.9
	1950.4	1.0	25.7	1733.7	1.0	35.7
	1959.3	1.0	3.9	1744.6	1.0	7.7
ν_4				522.7	1.0	2.3
	628.3	1.0	2.7	523.7	1.0	3.9
				531.1	1.0	2.3
	638.2	1.0	6.1	532.5	1.0	9.4
	658.3	1.0	1.7	536.3	1.0	4.3
				540.9	1.0	0.3

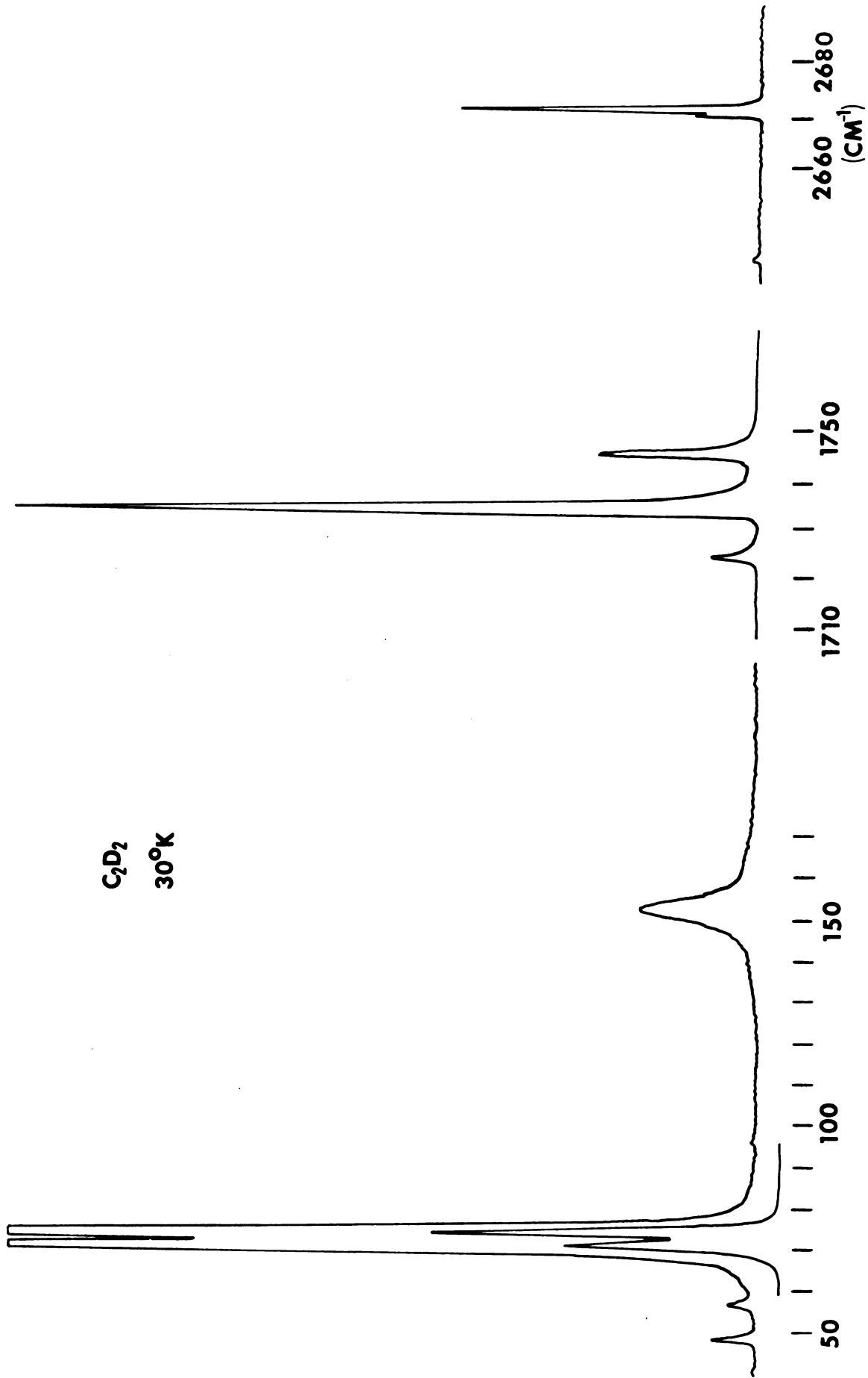
a. Normalized to first two intensities = 100.

b. Instrumental resolution = 1.0 cm⁻¹ (laser linewidth).

c. Two components not resolved well enough to list separately.

Figure 27

Raman spectrum of α C₂D₂ (30°K).



of C_2D_2 is shown under high resolution in Figure 28. Instead of the predicted four components of ν_4 (three were observed in C_2H_2) there are now six components; however the highest frequency one may be due to ν_4 of C_2HD .⁵⁴ Figure 29 shows the matrix isolated spectrum of C_2H_2 in C_2D_2 , again showing the lattice region (essentially unchanged from pure C_2D_2), ν_2 of C_2D_2 showing three components as before, ν_2 of C_2H_2 now isolated and unsplit (not factor group coupled), ν_1 of C_2D_2 as before except now (at 50°K) the two factor group components are less resolved, and the isolated unsplit ν_1 of C_2H_2 . Figure 30 has the ν_4 of C_2D_2 (expanded on top line) essentially unchanged from pure C_2D_2 except for a small low frequency shoulder, and the isolated ν_4 of C_2H_2 now split into an approximate doublet, demonstrating the site effect (D term) without the factor group coupling (M term). Figure 31 shows two different concentrations of C_2D_2 (5% and 1.5%) isolated in C_2H_2 . The lattice region is unchanged from pure C_2H_2 , ν_2 of C_2D_2 is now an isolated singlet, ν_2 of C_2H_2 again shows the three components as when pure, ν_1 of C_2D_2 is an isolated singlet and ν_1 C_2H_2 is the doublet (plus C^{13}) as in the pure solid. Figure 32 has ν_4 (at 5% and 1.5% of C_2D_2) for both C_2D_2 and C_2H_2 . ν_4 of C_2D_2 now shows four components (the weak one at highest frequency is again assigned as ν_4 of C_2HD) instead of the expected two, and ν_4 of C_2H_2 has the three components as in the pure solid.

Figure 28

Raman spectrum of ν_4 C_2D_2 (α phase at 30°K).

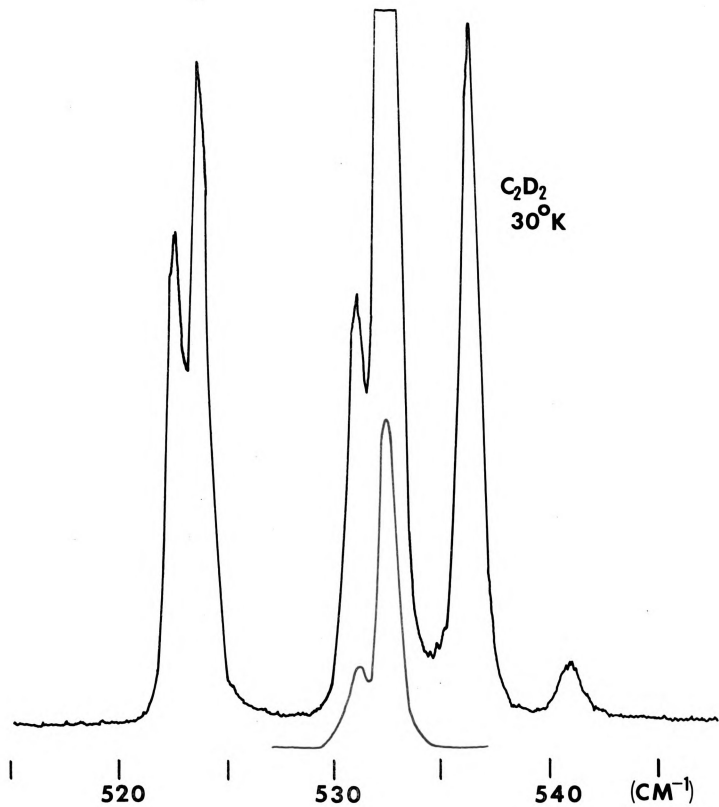


Figure 29

Raman spectrum of 5% C_2H_2 isolated in C_2D_2 at 50°K.

Figure 30

ν_4 of Raman spectrum of 5% C_2H_2 isolated in C_2D_2 at 50°K.

Figure 31

Raman spectra of 5% and 1.5% C_2D_2 isolated in C_2H_2 .

5% C₂H₂ in C₂D₂

50°K

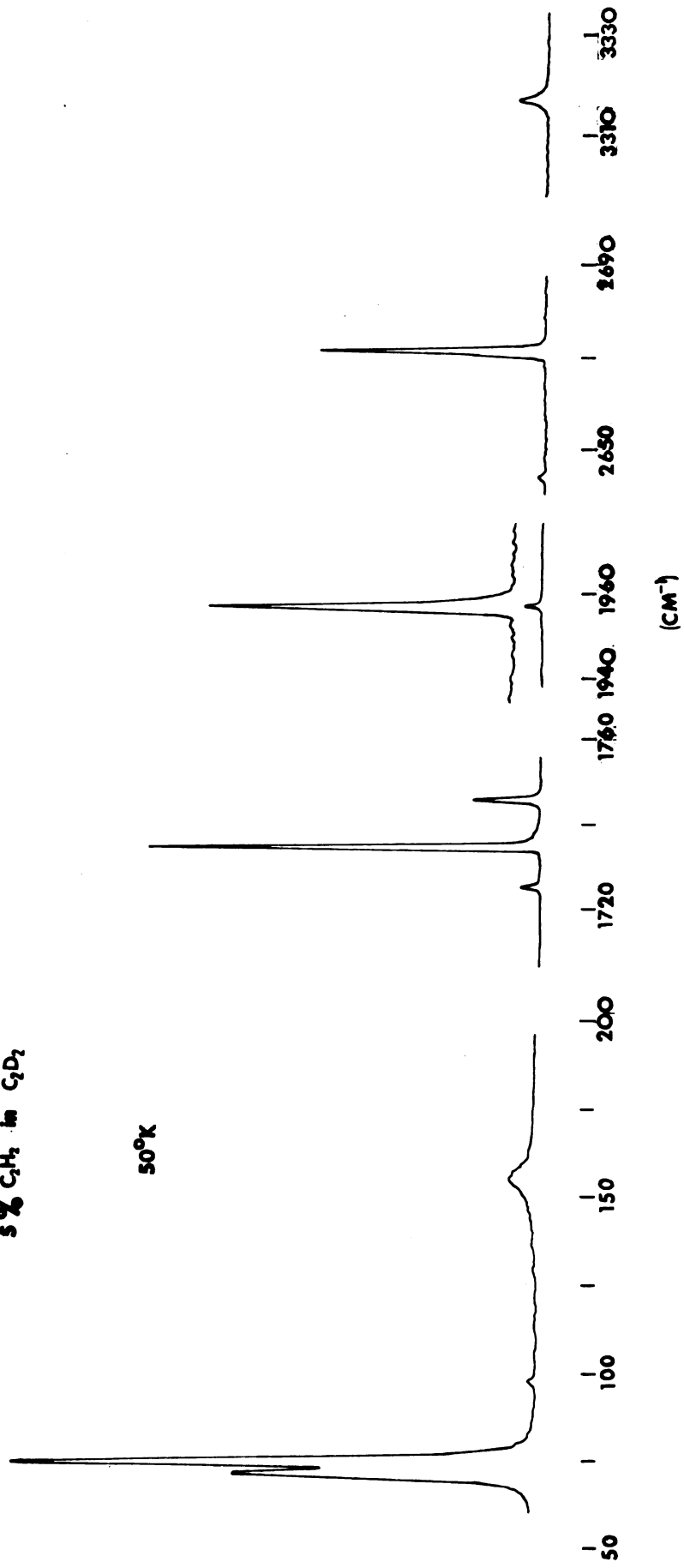


Figure 32

ν_4 of Raman spectrum of 5% and 1.5% C_2D_2 isolated in C_2H_2 at 50°K.

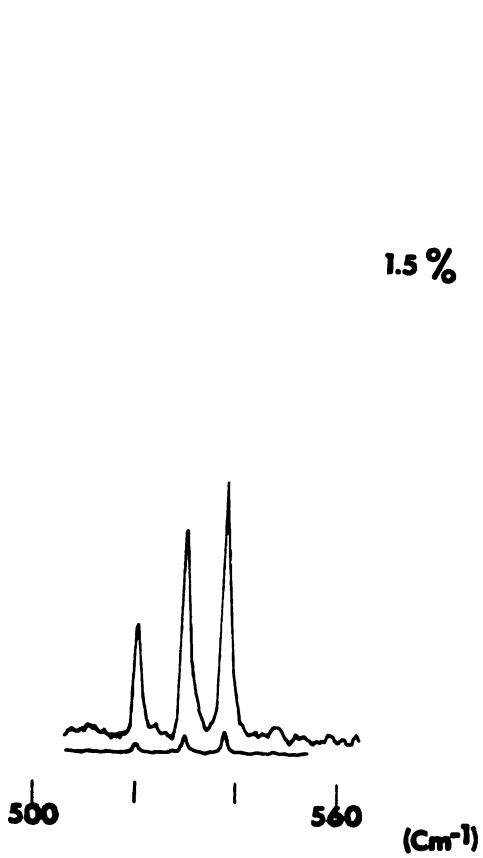
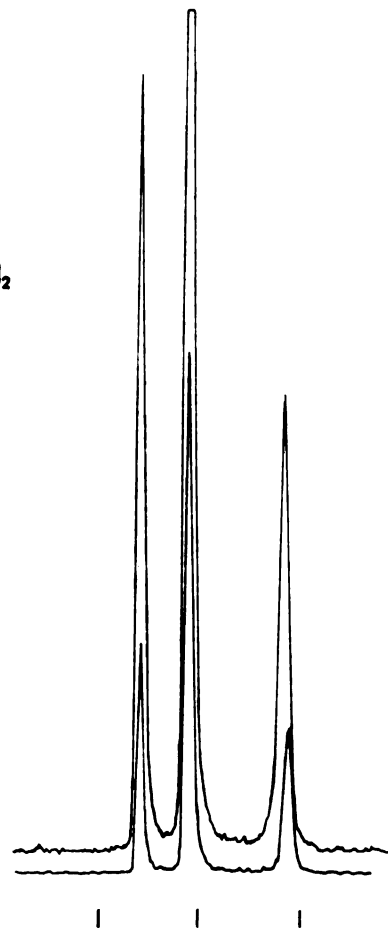
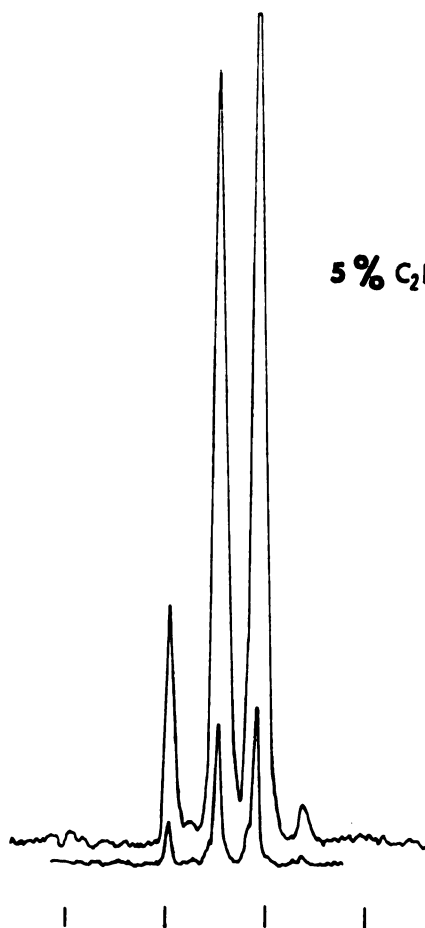


Figure 33 shows the higher temperature (above 133°K) β phase spectrum of pure C_2H_2 showing two lattice modes (of the three expected), two (of the expected three) components of ν_4 (three including the asymmetry of the larger lower frequency mode), three components of ν_2 (the two predicted plus C^{13}), and the two predicted components of ν_1 . Figure 34 shows the analogous warmer phase of pure C_2D_2 . The sharp features at approximately 20, 30 and 50 cm^{-1} are grating ghosts superimposed on the two broad lattice modes, and ν_1 is not split as before (it was only barely resolvable in α C_2D_2), the ν_2 and ν_4 regions are completely analogous to those of C_2H_2 . Table XX lists the peak frequencies, widths at half height and intensities of the warmer temperature phase of C_2H_2 and C_2D_2 . Table XXI lists the peak frequencies of the mixed crystal spectra of C_2H_2 and C_2D_2 .

From Table XXI we see that ν_1 isolated of C_2H_2 lies within experimental error (± 1.0 cm^{-1}) of the midpoint of the pure crystal peaks (ignoring C^{13} of course). The gaseous frequency of ν_1 is 3373.7 cm^{-1} .²⁴ Thus at the site of the crystal (plus any temperature effect) the frequency of ν_1 is shifted down to 3317.1 cm^{-1} . Similarly for C_2D_2 ν_1 shifts from 2700.5 in the gas to 2671.1 cm^{-1} at the crystal site. Then factor group coupling (the M term in the Interpretation section) splits the vibration symmetrically about this site frequency by 9.2 cm^{-1} in C_2H_2 and ≤ 1.0 cm^{-1} in C_2D_2 . The symmetric splitting would come from the (harmonic) part of M that deals with exchange of vibrational energy with non-translationally equivalent nearest neighbors

Figure 33

Raman spectrum of higher temperature (β) phase of C_2H_2 at $175^\circ K$.

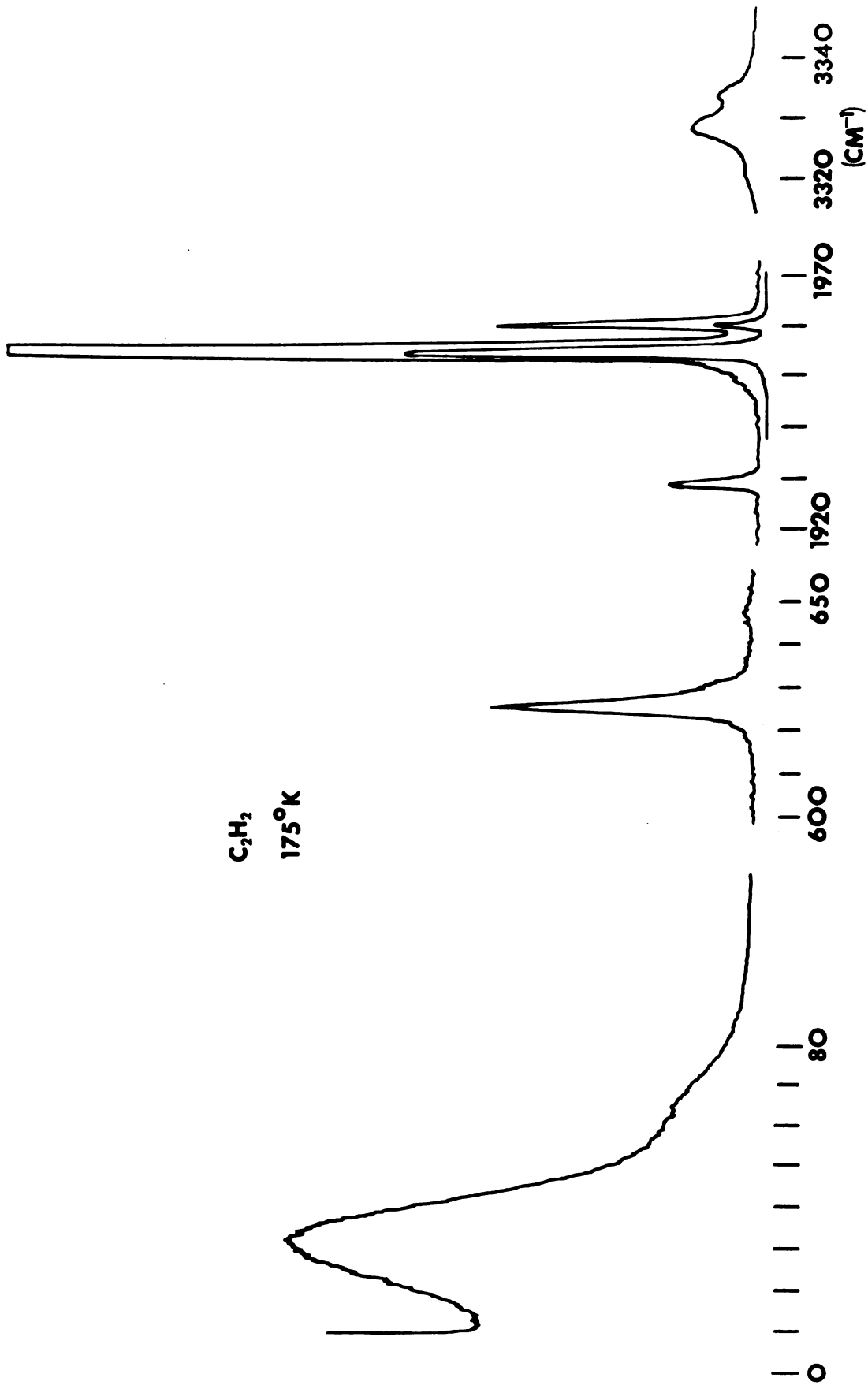


Figure 34

Raman spectrum of higher temperature (β) phase of C_2D_2 at 160°K

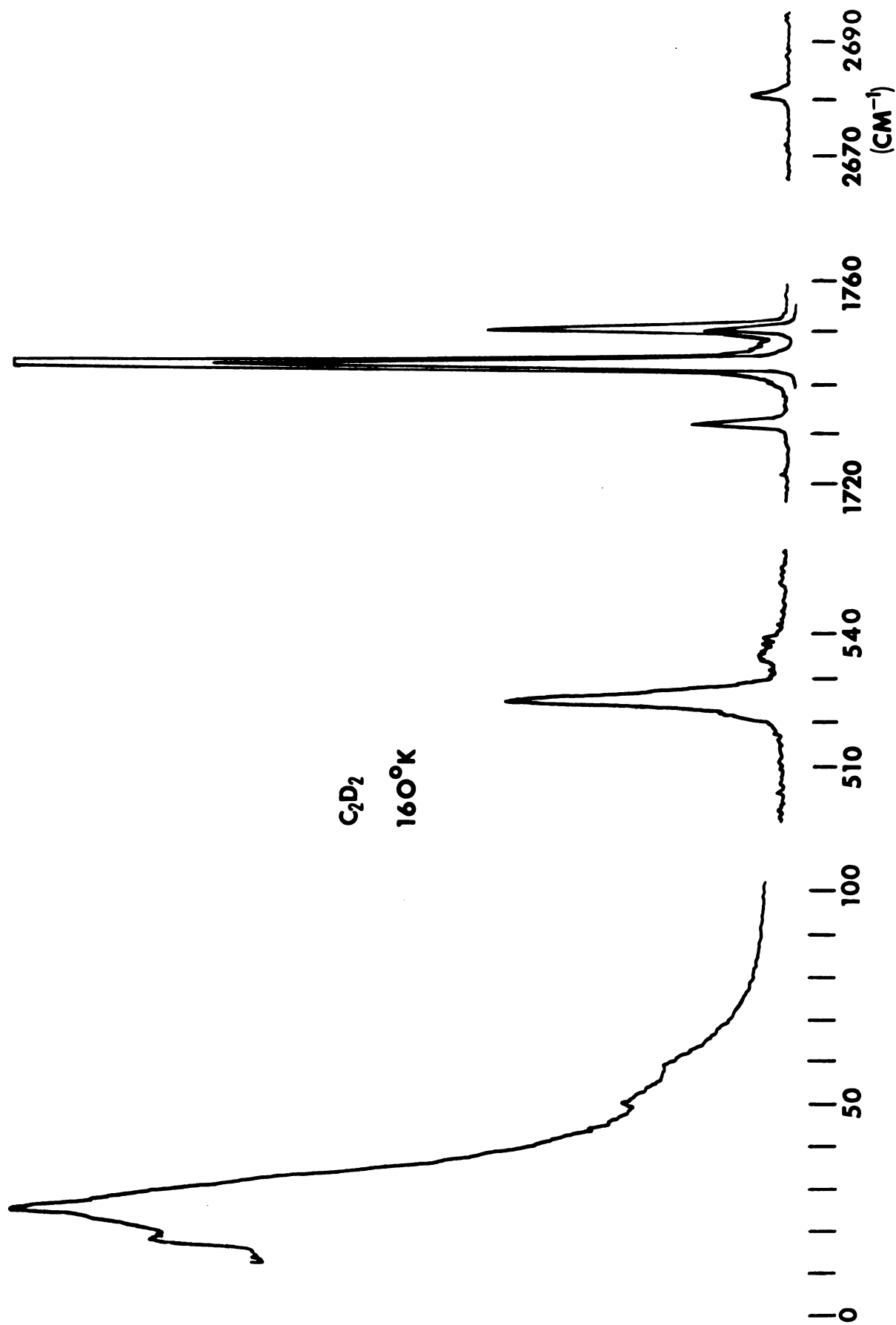


Table XX

Frequencies and intensities of higher temperature phase of C_2H_2 and C_2D_2 .

C_2H_2 ($T=166^\circ K$)				C_2D_2 ($T_2=168^\circ K$)		
Assignment	Frequency (cm^{-1})	Half-width ^a (cm^{-1})	Intensity ^b	Frequency	Half-width	Intensity ^b
Lattice	30.7	$\sim 35.$		25.1	~ 25	
	66.8	c		59.7	c	
ν_1	3327.6	~ 5.5	6.9	2681.0	1.5	10.
	3332.8	~ 4.5	3.1			
ν_2	1928.4	1.5	2.5	1732.3	1.0	15.7
	1954.7	1.0	74.8	1743.2	1.0	89.0
	1960.2	1.0	7.7	1750.1	1.5	48.0
ν_4	624.8	3.5	7.7	524.9	3.5	85.7
	647.0	c	0.3	535.9	6	5.3

a. Instrumental resolution = 1.0 cm^{-1} .

b. Normalized to $\nu_1 = 10.0$

c. Wide

Table XXI

Mixed crystal frequencies of C_2H_2 and C_2D_2 at 50°K.

C_2H_2				C_2D_2		
<u>Assignment</u>	<u>Host</u>	<u>Isolated</u>	<u>Gas</u> ^a	<u>Host</u>	<u>Isolated</u>	<u>Gas</u> ^a
Lattice	83.0			71.9		
	87.4			75.2		
	174.0			155.1		
ν_1	3305.4 ^b					
	3312.8	3317.1	3373.7	2671.9	2671.7	2700.5
	3322.0					
ν_2	1926.0 ^b			1724.9 ^b		
	1950.8	1957.0	1973.8	1734.6	1742.2	1762.4
	1959.2			1745.6		
ν_4	628.8			523.0		
		645.8	611.8	524.3	521.4	
	638.5					
		653.9		531.1	530.6	505.
	657.8			532.5	538.4	
				535.6		
				540.6 ^c	547.8 ^c	

a. Room temperature data from ref. 24.

b. C^{13} isotope peak.c. Tentatively assigned as ν_4 of C_2HD (see ref. 54).

while any asymmetry to the splitting (in this case very small) would come from exchange of vibrational energy with translationally equivalent (non-nearest) neighbors. The large (order of magnitude) change in the magnitude of the factor group splitting between C_2H_2 and C_2D_2 can be explained best by the fact that it appears for hydrogenic modes the dominant form of the perturbing potential is a hydrogen-hydrogen repulsion term.⁶⁵ With this type of potential, the factor group splitting is controlled by the amplitude of the C-H vibration. This amplitude will be smaller in the deuterated case both because of the significant increase in mass of the deuterium and because of the additional mixing of $C\equiv C$ character into the C-D stretching normal mode of C_2D_2 (see the following discussion of intensities for the normal coordinate eigenvectors). Thus it is reasonable for the coupling to be much smaller in the deuterated case. Unfortunately, ν_2 does not follow the predictions of this model as well. The isolated ν_2 of C_2H_2 occurs at 2.0 cm^{-1} above the midpoint of the two factor group coupled modes which are themselves only 8.4 cm^{-1} apart. Similarly ν_2 of C_2D_2 isolated is 2.1 cm^{-1} above the average of the two factor group coupled modes which are 11.0 cm^{-1} apart. This would indicate significantly larger contribution from the non-nearest neighbors (frequency shifting) part of M. Since we do not know the form of the perturbing potential that would be appropriate for this mode, we cannot conclude whether this is reasonable or not. However, one would expect the contributions of non-nearest neighbors (translationally

equivalent) to be greater for a mode such as ν_2 , since ν_2 is not as likely to be dominated by the repulsive part of the interaction potential. However, it is likely that the assumption of a center-center perturbation potential is not very meaningful in this type of crystal, and that electronic overlap between molecules is significant, and under these conditions the model would not be useful. The ν_4 splittings cannot be successfully interpreted for either isotope, since in C_2H_2 one of the four predicted modes is not observed, and in C_2D_2 both the pure crystal and the isolated molecule shows at least one unpredicted band. In the isolated ν_4 of C_2H_2 however, we do clearly see the two-fold degeneracy lifted by the site by approximately 8 cm^{-1} .

Table XXII lists the experimental (gas phase) values for the squares of the mean values $[(\bar{\alpha}')^2]$ and anisotropies $[(\bar{\gamma}')^2]$ of the polarizability derivative matrix associated with ν_1 and ν_2 of C_2H_2 ⁶² and the magnitude of $(\alpha_{||} - \alpha_{\perp})$,⁶³ that is the absolute value of the difference between the polarizability parallel to the (linear) molecular axis and the polarizability perpendicular to the molecular axis.

Table XXII

Gas phase polarizability data for C_2H_2 ^{62,63}			
Band	$(\bar{\alpha}')^2 (\frac{\text{cm}^4}{\text{g}})$	$(\bar{\gamma}')^2 (\frac{\text{cm}^4}{\text{g}})$	$(\alpha_{ } - \alpha_{\perp}) (\text{\AA}^3)$
ν_1	0.88	2.61	
ν_2	2.48	1.20	
Lattice Librations	0.0	1.45	1.86

The expression for the intensity of a Raman transition is given by⁶⁶

$$I = \frac{K'(\nu_0 - \nu)^4 g}{\nu[1 - \exp(-h\nu/kT)]} [4.5(\bar{\alpha}')^2 + (\gamma')^2]$$

where K' is a constant, ν_0 the frequency of incident exciting radiation, ν the frequency of the transition, h Planck's constant, k the Boltzmann constant, and T the temperature ($^{\circ}\text{K}$). g is the degeneracy of the transition, $\bar{\alpha}'$ and γ' are the mean value and anisotropy of the polarizability derivative matrix, and $g[4.5(\bar{\alpha}')^2 + (\gamma')^2]$ is called the scattering activity. This equation assumes Placzek's polarizability theory is valid,⁶⁶ and that we are irradiating a polycrystalline sample with polarized light.⁶⁷

With the gas phase data, and the moment of inertia of the molecule, one can calculate the relative and total intensities of the various fundamental components and librational modes by calculating the scattering activity $[g[4.5(\bar{\alpha}')^2 + (\gamma')^2]]$ of the various modes. For the internal modes, the total scattering activity comes directly from the above data, while for the librational modes, Cahill⁶⁷ has developed the general expressions for the relative scattering activities as well as their total intensities. These are calculated by construction of unit cell symmetry coordinates and differentiation of the unit cell polarizability (assumed to be the sum of the gaseous molecular polarizabilities contained in the unit cell) with respect to each of the unit cell symmetry coordinates. Since this procedure has already been written up in complete detail^{57,67} for the crystal structure of interest, I will include only the results.

The total scattering activities (calculated and observed) are listed in Table XXIII.

Table XXIII

Total scattering activities observed and calculated for C_2H_2 and C_2D_2 .

Scattering activities ($\frac{cm^4}{g}$)			
Band	calculated	observed C_2H_2	observed C_2D_2
ν_1	6.58	11.79	2.40
ν_2	12.36	12.36	12.36
ν_4		1.00	1.44
Librations	1.45	1.42	1.08

The change in observed total scattering activity of ν_1 compared to ν_2 (see Table XXIII) for the deuterated compound was anticipated as a result of different amounts of mixing of the internal coordinates that comprise these normal modes. This was borne out by the calculated eigenvectors listed in Table XXIV; however use of these eigenvector coefficients along with the gas phase bond polarizabilities⁶² predict a much greater change than observed (see Table XXIV).

Table XXIV

Eigenvectors and ratios of total Raman intensities of ν_1 and ν_2 of C_2H_2 and C_2D_2 .

$q_1 = q_2 = \text{C-H internal coordinates; } q_3 = \text{C}\equiv\text{C internal coordinate}$				
	<u>eigenvectors</u>		<u>ratios of scattering activities ν_1/ν_2</u>	
	ν_1	ν_2	<u>calculated</u>	<u>observed</u>
C_2H_2	$0.7221(q_1+q_2)$ $-0.1802 \quad q_3$	$0.1278(q_1+q_2)$ $+0.3663 \quad q_3$	0.61	0.95
C_2D_2	$0.4869(q_1+q_2)$ $-0.3012 \quad q_3$	$0.2299(q_1+q_2)$ $+0.2756 \quad q_3$	0.012	0.19

Our errors in predicting the magnitude of this change in relative intensity of ν_1/ν_2 upon deuteration are probably due both to the inherent assumptions of the "bond polarizability"⁶⁸ concept and to the fact that the transformation from internal coordinates to normal coordinates is not an orthogonal one.⁶⁹

In the structure appropriate for the lower temperature (α) phase of C_2H_2 , (D_{2h} factor group analogous to the halogens), there is an unknown parameter, θ in Figure 35 which can vary from 0 to 90° without changing the crystal structure. The relative scattering activity of the various modes will depend upon the value of the angle θ . Table XXV lists the relative scattering activity for ν_4 and the librations

Figure 35

Primitive unit cell of halogen structure (α -C₂H₂) showing crystal axes (Y,Z) and molecular axes (y_o, z_o). X and x_o are coincident and directed out of plane of paper for molecule at origin.

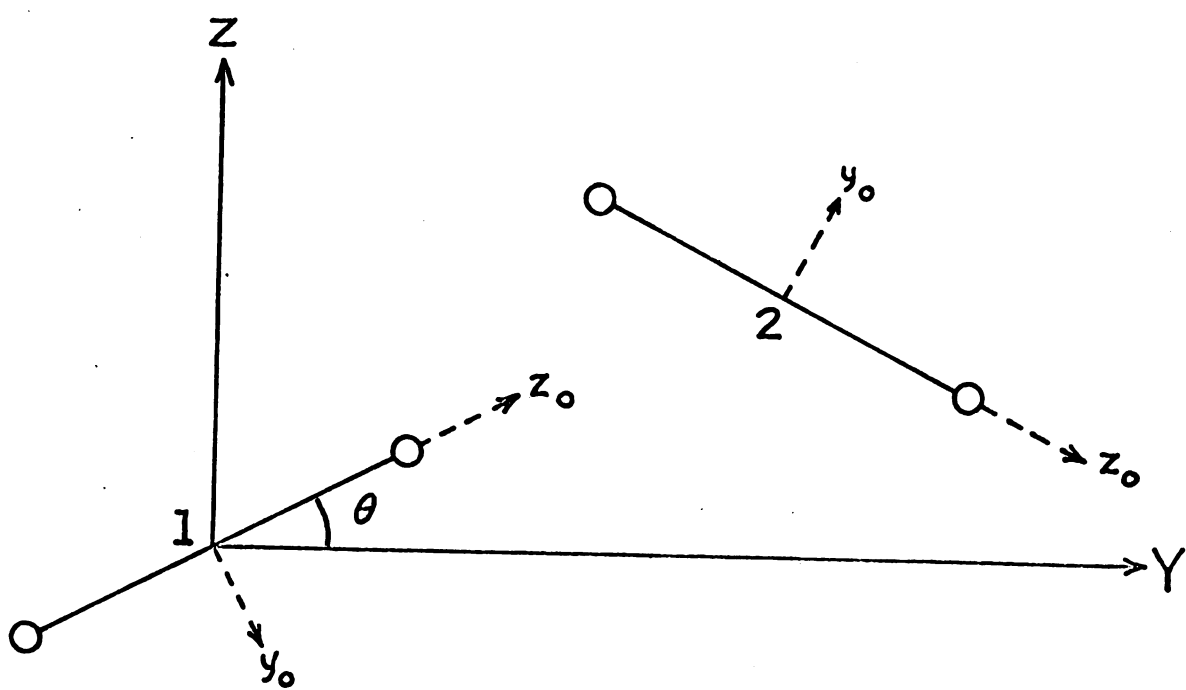


Table XXV

Relative scattering activities of the components of ν_4 and the librations.

<u>Calculated relative scattering activities</u>				
(degrees)	A _g	B _{1g}	B _{2g}	B _{3g}
0	0.	1.	0.	1.
10	.117	.970	.030	.884
20	.413	.884	.117	.589
30	.750	.750	.250	.250
35	.881	.670	.329	.116
40	.970	.587	.413	.030
45	1	.500	.500	0
50	.970	.413	.587	.030
55	.881	.329	.670	.116
60	.750	.250	.750	.250
70	.413	.117	.884	.589
80	.117	.030	.970	.884
90	0.	0.	1.	1.
<u>Observed</u>				
Lattice C ₂ H ₂	(87.4)	(83.6)	(174.9)	(cm ⁻¹)
	1.00	0.74	0.31	
C ₂ D ₂	(74.1)	(71.1)	(152.1)	(cm ⁻¹)
	1.00	0.74	0.57	
ν_4 C ₂ H ₂	(638.2)	(628.3)	(658.3)	(cm ⁻¹)
	1.00	0.43	0.29	
ν_4 C ₂ D ₂	(522.7)	(531.1)	(536.3)	(cm ⁻¹)
	(+523.7)	(+532.5)		
	1.0	0.52	0.37	

as a function of θ , and also the experimentally observed values. Table XXVI lists the ratio of scattering activities for the B_{3g} and A_g symmetry modes of the symmetric stretching (ν_1 and ν_2) fundamentals as a function of θ along with the observed experimental values.

From Table XXV we see that the experimental data appear to best fit an angle θ of 45° , although Ito's assignment⁵⁸ of the highest frequency lattice mode as being $2 \times A_g$ would also fit C_2H_2 reasonably well if $\theta = 0^\circ$. However, the increase in the highest frequency lattice mode intensity in C_2D_2 and the relative intensities of the components of ν_4 lead us to conclude an angle of 45° is more probable. This conclusion is supported by Table XXVI, where although no angle predicts the correct ratio of observed intensities of the factor group components of the ν_1 and ν_2 modes, they are closest to the predictions of an angle of 45° .

We thus feel that we have at least qualitatively explained all of the Raman spectral features observed with the exception of ν_4 of C_2D_2 . A different crystal structure appears unlikely because of the large amount of (infrared and Raman) spectroscopic data that is well explained by the present structure. No impurities, other than approximately 3% C_2HD were found in a mass spectroscopic analysis of the sample used. The possibility of C_2HD affecting the C_2D_2 spectra to cause the extra peaks (by site splitting but not factor group coupling with C_2D_2) also seems unlikely, since the unexplained peaks

Table XXVI

Calculated and observed ratios of scattering activities of the factor group components of ν_1 and ν_2 of α -acetylene.

ratio \ θ (degrees)		0	10	20	30	40	45	Observed	
								C_2H_2	C_2D_2
$B_{3g}/A_g \nu_1$	0		.0375	.145	.303	.428	.446	0.818	
$B_{3g}/A_g \nu_2$	0		.0080	.029	.054	.070	.072	0.103	0.123

did not grow in relative intensity upon addition of 5% C_2H_2 to the sample.

One possible, but rather unlikely explanation of the extra components of ν_4 involves the naturally abundant C^{13} acetylene ν_4 modes which might "borrow" intensity (as in Fermi resonance) from ν_4 bands of adjacent C_2D_2 molecules.

Conclusions

The Raman spectra of both crystalline phases of C_2H_2 and C_2D_2 have been recorded and interpreted by the corresponding "factor group" correlation diagrams. In the lower temperature phase, mixed crystal spectra of one isotope isolated in the other have been obtained and interpreted in terms of the site effect without factor group coupling.

In the lower temperature phase, where the crystal structure is not certain, our data agrees well with the proposed structure^{55,56,58} in all places except ν_4 of C_2D_2 . The two unexpected additional components of ν_4 of C_2D_2 have not yet been adequately explained.

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