

THE INFRARED AND RAMAN SPECTRA OF REALGAR AND ORPIMENT

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ABSTRACT

Far infrared absorption and laser-excited Raman spectroscopy can be easily applied to the investigation of minerals and are extremely useful for structural studies and identification purposes, especially for crystals containing heavier atoms. It is only necessary to have the crystals ground to a powder. The powder is used directly to obtain Raman spectra and as an ordinary mull for the far infrared. If a single crystal or a cluster of small crystals is available, a Raman spectrum can be obtained without any preparation at all. These points are exemplified by the spectra of As_4S_4 (realgar) and As_2S_3 (orpiment). The observed spectrum of realgar is tentatively assigned to an As_4S_4 molecule of the cradle type, possessing D_{2d} symmetry. The As-S stretching and S-As-S bending regions are identified for orpiment.

INTRODUCTION

Although mid-infrared absorption spectroscopy ($4000\text{--}200\text{ cm}^{-1}$) has been frequently employed in the study of inorganic compounds and natural minerals, the application of far infrared absorption and of Raman scattering techniques to these studies has been much more limited. Spectra have been obtained in the mid-infrared of the common silicate, oxide, sulfate, phosphate, and carbonate minerals. These spectra usually show a few absorption peaks, often broad, corresponding to vibrations involving motions of the oxygen atoms. Minerals containing heavier atoms were seldom studied because their vibrational absorption fundamentals are expected to occur in the far infrared region ($200\text{--}10\text{ cm}^{-1}$). As to Raman spectroscopy, the main reason that prevented its application to the study of minerals was the difficulty of handling solid samples. Examples of this situation can be found in the extensive survey of mid-infrared absorption spectra of inorganic compounds by Miller and Wilkins (1952) (NaCl region) and by Miller *et al.* (1960) (CsBr region) and in the critical bibliography on the studies of minerals in the infrared by Lyon (1962). No similar publications are available for the far infrared and for the Raman effect, and this simply reflects the fact that there have been very few papers on the far infrared and Raman spectra of minerals. The present availability of commercial far-infrared spectrometers, and the recent introduction of lasers as exciting sources for Raman scattering, will certainly change this situation in the near future.

This paper presents the application of these two techniques to the

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study of two arsenic sulfide minerals: realgar and orpiment. The observed spectra are interpreted qualitatively on the basis of the structures which are known from electron and X-ray diffraction studies. This is more successful for realgar than for orpiment. When this work was started, its aims were more ambitious because it was hoped that a quantitative interpretation of the spectra would be possible. For this purpose, however, additional experimental data would have been necessary, such as Raman polarizations. The crystallites were too small to use single-crystal techniques, and no suitable solvents were found for solution methods. Also the melting points of the samples were too high for the melts to be handled with the techniques at our disposal. Attempts were also made to apply a high pressure microsampling technique (Lippincott *et al.* 1966) which might provide a means of distinguishing between lattice and internal vibrations. Even a few atmospheres pressure, however, turned the samples too dark to give a Raman spectrum with excitation by 6328 Å He-Ne laser radiation.

The molecular structure is known from electron diffraction studies of the gases (Lu and Donohue 1944). The structure of realgar was determined by X-ray diffraction by Ito *et al.* (1952), and of orpiment by these same authors and by Morimoto (1954), as shown in Figure 1. For As_4S_4

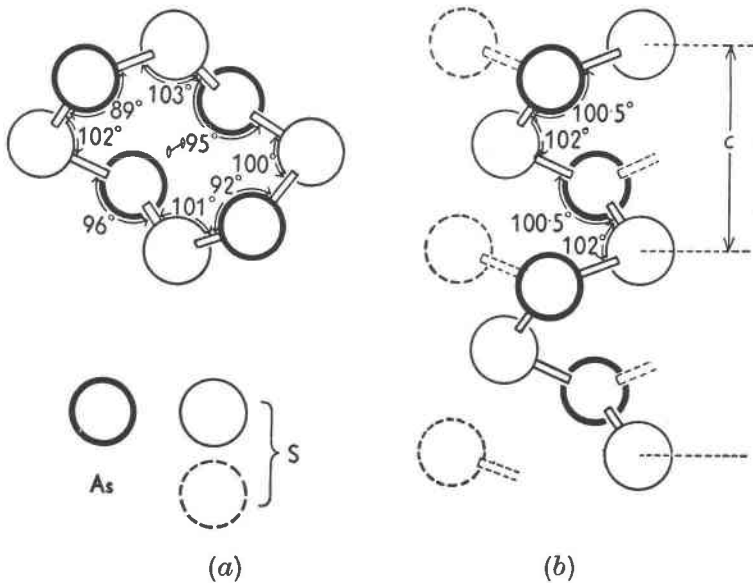


FIG. 1. Molecular structures of (a) realgar and (b) orpiment. In (b) is shown an As_2S_2 spiral chain (heavy and light full circles), and an As_2S_3 layer (full and broken circles). Reproduced from Ito, Morimoto and Sadanaga, 1952).

in the vapor, the structure is similar to that of nitrogen tetrasulfide. The crystal is built up of separate As_4S_4 molecules of the cradle type, and the space group is $C_{2h}^5-P2_1/n$. The molecular symmetry is D_{2d} . Four S and four As atoms in the molecule are bound to one another by covalent bonds, forming a square and a tetrahedron, respectively. The square of sulfurs cuts through the middle of the arsenic tetrahedron. Orpiment, on the other hand, is made up of superimposed As_2S_3 layers containing AsS spiral chains. The space group is the same as for As_4S_4 . Lu and Donohue (1944) suggested that the orpiment molecule in the vapor is As_4S_6 and that it possesses an As_4O_6 structure.

Glasses having the composition As_2S_3 , or produced using this molecule as a network former and different sulfides as network modifiers, have had their mid-infrared absorption spectra determined by several authors, including Frerichs (1953), Matsuda (1960) and Vashko *et al.* (1962). The purpose of these studies was to look for infrared transparent glasses. The spectra were not interpreted, since, as will be seen in the following, the fundamental vibration bands for the arsenic sulfides are expected to fall below 400 cm^{-1} . A table of the positions of the observed infrared bands down to 400 cm^{-1} was, however, given by Vashko *et al.* (1962) for As_2S_3 , As_2Se_3 , and other glasses.

A very recent paper by Ward (1968) gives the Raman spectra of natural specimens of realgar and orpiment and of glasses having a similar composition. However no infrared spectra were obtained, and no interpretation of the observed spectra was attempted. Our Raman results agree very well with his.

A knowledge of the spectra of related molecules, such as the arsenic oxides, would have greatly helped in the interpretation of the spectra of realgar and orpiment, if suitable correlations could be established between the spectra of corresponding molecules. Arsenic oxides were studied, to a limited extent, especially by Russian authors. For instance Cheremisinov (1959) obtained the infrared and Raman spectra of the low temperature form of crystalline arsenic trioxide (octahedral) and gave an interpretation based on an As_4O_6 dimer molecular species of T_d symmetry. This symmetry was chosen by a simplified method of counting the observed Raman and infrared bands, and checking for coincidences. However, according to Ito *et al.* (1952) there are two arsenic oxide minerals whose structures are related, in a similar way, to the structures of realgar and orpiment. Arsenolite (As_2O_3) is made up of As_4O_6 groups of the cradle type, like realgar, with two more oxygen atoms attached on top and at the bottom, while claudetite (As_2O_3) has a layer structure like that of orpiment. The mode of linkage in these two minerals, if oxygen and sulfur atoms are looked upon as equivalent, is roughly the same.

We were unable to establish a correlation between the vibrational spectra of realgar as presented in this paper, and the spectra of arsenic trioxide of Cheremisinov. The spectra are quite different. On the other hand, the vibrational spectrum of monoclinic claudetite (As_2O_3), that possesses a molecular structure similar to orpiment, is not known.

EXPERIMENTAL

The samples of the realgar and orpiment minerals used in this investigation were purchased from a mineralogical supply service and came from near Manhattan, Nevada. Since the realgar mineral contained some orpiment and vice-versa, the small crystals used were selected under a magnifier. The crystals were ground to a powder with a dentist's amalgamator.

The Raman spectra were obtained with a Cary 81 spectrometer and excited with a Spectra Physics model 125 He-Ne laser delivering 50 mw of power at 6328 Å. Instead of employing the regular sample holder for compressed powders, it was found more convenient to use a glass capillary with end-on illumination as customarily employed for liquids (Hawes *et al.* 1966). The capillary was loosely packed with the powder. During the irradiation no changes were observed in orpiment (As_2S_3), but realgar (As_4S_4) changed slowly from red to yellow. This produced small changes in the spectra of the samples of realgar irradiated for long time since some weak bands started to appear at the positions of the strongest orpiment bands. An irregular chunk of realgar of approximately one centimeter cube was also irradiated by the laser beam. The beam was concentrated in a small region of clustered crystals. Excellent Raman spectra were obtained in this way. The background, for instance, was weaker in this case than for the powdered samples. The diameter of the He-Ne laser beam at the sample is approximately 2 mm. The tiny realgar crystals that accumulate in small clusters in the natural minerals have an approximate area of 0.4 mm². For this reason no oriented single crystal study could be carried out. Except for minor changes in the intensities of some of the bands, the Raman spectrum of the clustered crystals coincided with the spectrum of the powder.

Infrared spectra of nujol mulls were obtained from 400 to 35 cm⁻¹ using thin films of sample pressed between 1/8 in. thick polyethylene plates. A Beckman IR-11 far infrared spectrophotometer was employed.

The observed spectra are shown in Figures 2 and 3. The wave number values of the observed bands are given in Tables 1 and 2. The accuracy is approximately ± 2 cm⁻¹ for Raman bands and ± 3 cm⁻¹ for infrared bands.

RESULTS AND DISCUSSION

Both molecules studied are extremely strong scatterers and good infrared absorbers. As can be seen from the figures most of the observed bands are narrow and well defined. We will now attempt a qualitative assignment of the observed frequencies to the normal modes of vibration.

There are only two related molecules that have been spectroscopically analyzed previously that can be of some help in the discussion which follows. The first is the only arsenic sulfide that has had its spectrum assigned, namely the AsS_4^{2-} ion. It was studied in the Raman by Siebert (1966), and the four observed frequencies were assigned to T_d symmetry as follows: As-S stretches: 419 cm⁻¹ (class F_2) and 386 (A_1) and angle de-

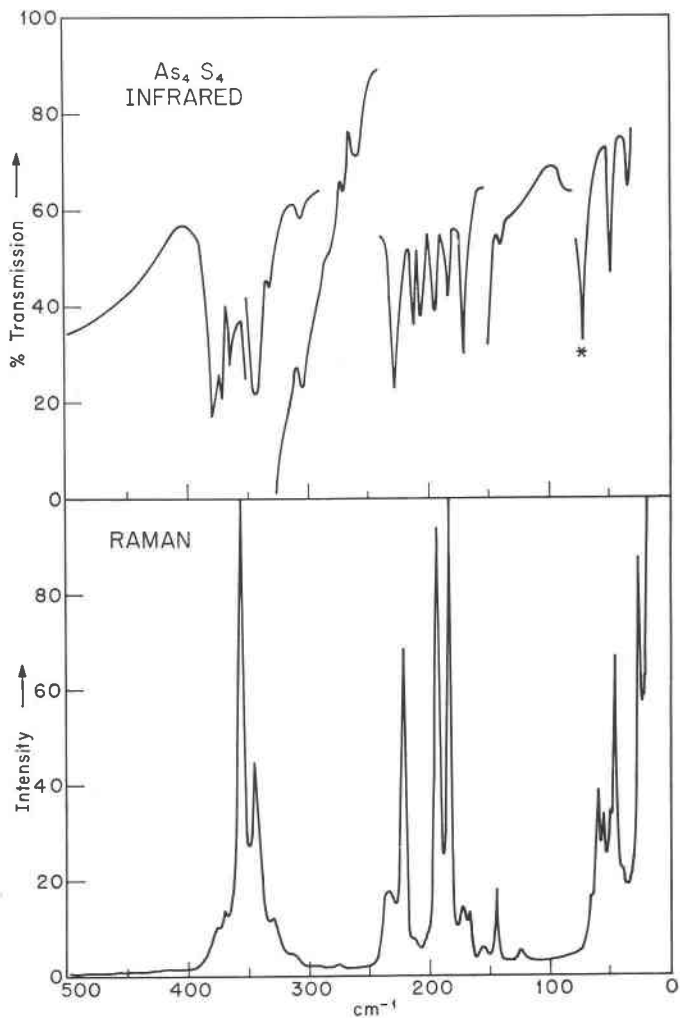


FIG. 2. Infrared and Raman spectra of realgar (As_4S_4). The infrared spectrum is a retrace of the original. A polyethylene band is indicated by *. Breaks in the infrared spectra curves are due to changes of sample thickness.

formations 216 (F_2) and 171 (E). One sees then that As-S stretching modes are expected around 400 cm^{-1} while S-As-S angle deformations fall in the neighborhood of 200 cm^{-1} . The other molecule is nitrogen tetrasulfide (N_4S_4). It was investigated spectroscopically in the Raman and infrared by Lippincott and Tobin (1953), and more recently by Bragin and Evans (1969). These last mentioned authors interpret their result;

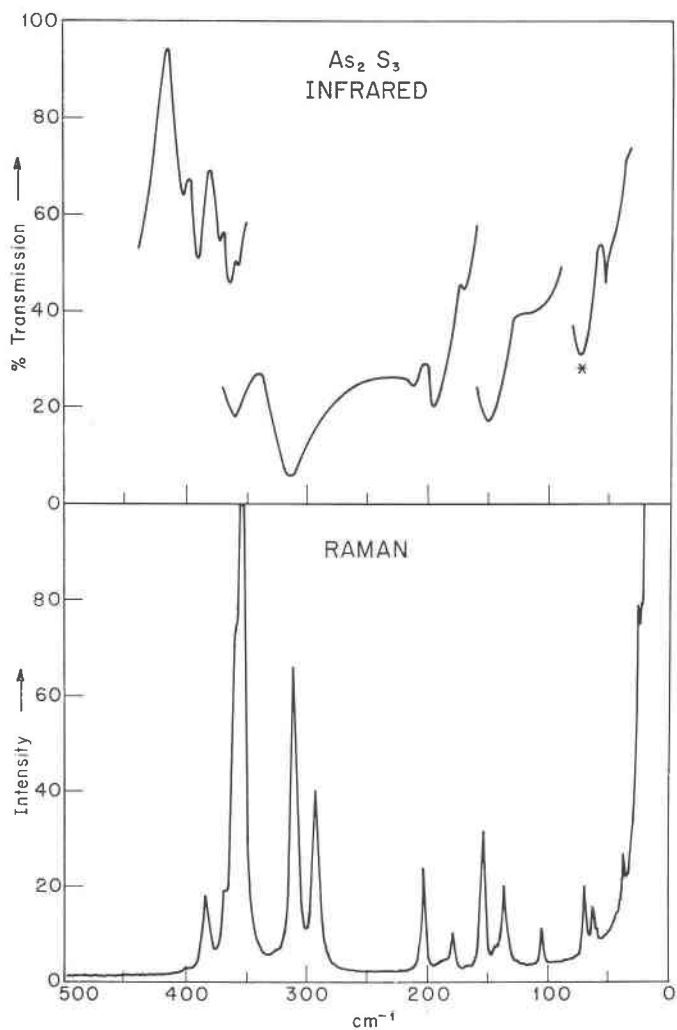


FIG. 3. Infrared and Raman spectra of orpiment (As_2S_3). The infrared spectrum is a retrace of the original. A polyethylene band is indicated by *. Breaks in the infrared spectra curves are due to changes of sample thickness.

based on the molecular model of Sharma and Donohue (1963) in which the S and N atoms alternate in an eight-membered cradle-shaped ring of D_{2d} symmetry, and in which the nitrogen atoms are coplanar. In the discussion which follows the realgar and orpiment molecules will be treated separately.

TABLE 1. OBSERVED INFRARED AND RAMAN SPECTRA OF REALGAR (As₄S₄)

Raman (powder)		Infrared (mull)		Interpretation
cm ⁻¹	Intens.	cm ⁻¹	Intens.	
19	vw			
23	vw			
26	s			
40	vw, sh	37	vw	
46	s	47	w	molecular bend (B ₂)
50	m			
55	m			
60	s			molecular bend (A ₁)
66	w, sh			
124	vw			2×60=120
143	m	141	vw	S-As-S bend (B ₂)
		148	vw	194-46=148
155	vw			222-66=156
166	m			222-60=162
172	m	170	s	S-As-S bend (E)
183	vs	183	m	S-As-S bend (A ₁)
193	vs	194	m	S-As-S bend (B ₁)
		205	m	143+60=203
214	vw	211	m	183+26=209
				170+46=216
222	vs	225	s	S-As-S bend (E)
235	m			50+183=233
				194+46=240
		258	vw	60+193=253
		269	vw	46+222=268
				50+225=275
276	vw	284	vw, sh	60+225=285
				143+170=313
313	vw			As-S stretch (B ₁)
329	w	330	m	As-S stretch (B ₂)
345	s	343	vs	As-S stretch (A ₁)
355	vs	358	m	As-S stretch (E)
370	w	367	s	As-S stretch (E)
376	w	373	s	As-S stretch (E)
416	vwv			60+355=415
445	vwv			2×222=444
460	vwv			46+193+222=461
526	vwv			194+330=524
556	vwv			194+358=552
591	vwv			225+367=592
696	vwv			2×345=690
735	vwv			2×367=734

w, m, s=weak, medium, strong.

v=very, sh=shoulder.

TABLE 2. OBSERVED INFRARED AND RAMAN SPECTRA OF ORPIMENT (As_2S_3)

Raman (powder)		Infrared (mull)		Interpretation
cm^{-1}	Intens.	cm^{-1}	Intens.	
23	vw			
26	w			
36	m			
		52	w	
59	vw, sh			
61	m			
69	m			
105	m			
136	m			
143	vw	139	vs	
154	s			
166	vw, sh	160	vw	$61+105=166$
179	m	183	m	
186	vw, sh			$36+154=190$
203	s	202	vw	
293	s			
311	s	305	s	
326	vw			$154+179=333$
		348	m	
355	vs	354	m	
360	m, sh	361	m	
369	w			
384	m	381	w	
		393	w	
400	vw			$2 \times 203 = 406$
435	vvw, sh			$69+368=437$
458	vvw, sh			$105+355=460$
474	vvw			$179+293=472$
498	vvw, sh			$203+293=496$
587	vw			$203+384=587$
652	vw			$293+355=648$
685	vvw, sh			$305+381=686$
707	vvw			$2 \times 355 = 710$
730	vvw			$355+384=739$
783	vvw			$2 \times 393 = 786$

w, m, s=weak, medium, strong.

v=very, sh=shoulder.

Realgar (As_4S_4). As mentioned before, experimental evidence from other sources points towards a molecular symmetry of the D_{2d} point group for the individual As_4S_4 molecules. One then expects that the vibrational fundamentals will be distributed as follows $3A_1+2A_2+2B_1+3B_2+4E$. All

but the A_2 modes should be active in the Raman spectrum, while only the B_2 and E modes should be active in the infrared. The space group for realgar is, however, C_{2h}^5 with only C_i available as site symmetry. The As_4S_4 molecules do not have a center of symmetry and must lie on sites of C_1 symmetry. As consequence all frequencies should become active. It should be possible to find out to what extent this actually happens through examination of the spectra of the powders. Comparison with the spectra of the liquid or of solutions would be very useful in separating the frequencies of the internal modes from lattice modes, splitting of degenerate modes, and splitting under the factor group. Since no spectra of liquid or solutions are available, a considerable amount of arbitrariness will have to be exercised in our choice of fundamentals. As already mentioned, the accepted structure for the S_4N_4 , which is similar to realgar, possesses a square of nitrogen atoms. In the case of realgar, however, the square is made up of sulfur atoms, as shown by the X-ray diffraction study of Ito *et al.* (1952). These authors also determined that the distance between arsenic atoms in the crystal for pairs on the same side of the equatorial plane formed by the square of sulfur atoms is 2.59 Å. Since the van der Waals diameter for arsenic is 4.00 Å—much larger than the above mentioned distance—a certain amount of interaction must exist between pairs of opposite arsenic atoms.

By looking at the spectra of this compound, especially the Raman spectrum in Figure 2, one immediately sees that the strongest bands fall in three definitely limited wavenumber regions. Two regions are centered around 350 and 200 cm^{-1} respectively, and the other lies below 65 cm^{-1} . Taking into account the already mentioned frequencies observed by Siebert in the Raman spectrum of AsS_4^{2-} it can be seen that the first two groups of bands contain the As-S stretching (400 cm^{-1}) and S-As-S bending (200 cm^{-1}) modes, respectively. The bands lower than 65 cm^{-1} should be due to ring deformations and lattice vibrations. These ring deformations are expected to involve movement of the pairs of opposite arsenic atoms.

Schematically the As-S stretches are distributed as $A_1 + A_2 + B_1 + B_2 + 2E$, and the ring deformations as $2A_1 + A_2 + B_1 + 2B_2 + 2E$. In the high-frequency region, then, five As-S stretching vibrations are expected and five bands were observed. If the activities for D_{2d} symmetry were obeyed, three of the Raman bands should have corresponding infrared bands, and should belong to classes B_2 and E , while two of the Raman bands should have no corresponding infrared bands and so belong to classes A_1 and B_1 . Since all five strongest Raman bands have corresponding infrared bands (due to relaxing of the selection rules in the crystal), and since no polarization of the Raman bands is known, an assignment can be attempted

only by taking into account the relative intensities of the bands. In the Raman effect the strongest bands belong usually to totally symmetrical vibrations. The band at 355 cm^{-1} is therefore assigned to the A_1 species. Since 329 cm^{-1} does not correspond to a strong infrared band, it is assigned to the B_1 species. The very strong infrared band 343 cm^{-1} is assigned to B_2 , and the remaining strong infrared bands 367 and 373 cm^{-1} are assigned to E. This assignment follows the corresponding one of Bragin and Evans (1969) for S_4N_4 that relies on polarization observations of some of the strongest Raman bands and on a normal coordinate analysis.

As for the bending modes the assignment is more arbitrary since there are more bands than needed, all with medium or high intensity. Although there are some Raman bands that have no corresponding infrared counterparts (such as 166 and 235 cm^{-1}) they are not the most intense in the spectrum and, besides, as shown above, the D_{2d} molecular symmetry does not seem to hold strictly in the crystal. We prefer to assign the strongest Raman bands to fundamentals, and therefore attribute 183 , 193 , and 222 cm^{-1} , respectively, to the A_1 , B_1 , and E deformation modes. The latter corresponds to the 222 cm^{-1} Raman band. For the B_2 mode we choose the 143 cm^{-1} band because it is needed for the interpretation of three sum bands. Two deformations of species A_1 and B_2 are still to be assigned. They are modes in which the pairs of arsenic atoms, on the same side of the equatorial plane formed by the four sulfur atoms, move toward and away from each other. By analogy with S_4N_4 the frequencies are expected to be very low. Nine Raman bands are available below 66 cm^{-1} for these modes. The strongest (as in the case of S_4N_4) are assigned, namely, 46 to B_2 and 60 cm^{-1} to A_1 . The band assigned to B_2 has an infrared counterpart observed only in thick mulls.

Table 1 also shows that it is not difficult to explain most of the weak bands as due to binary combinations or harmonics. With few exceptions the selection rules for D_{2d} molecular symmetry are followed. These exceptions reflect the lower site symmetry.

Orpiment (As_2S_3). The interpretation of the vibrational spectrum is much more difficult in this case than for realgar since, as shown by Ito *et al.* (1952), the structure of orpiment is made up of superimposed As_2S_3 layers containing As-S spiral chains (Fig. 1). Each As atom is surrounded by three sulfur atoms, and each S atom is shared by two As atoms. The layers are held to one another by van der Waals forces. The crystal symmetry (C_{2h}^5) is the same as for realgar (Morimoto, 1954). As already mentioned, the conversion of realgar to orpiment is relatively easy; schematically it requires breaking the ring and the insertion of a sulfur

atom between each As-As pair. Ito *et al.* (1952), pointed out that although the structure of orpiment seems to have little similarity with that of realgar, on closer examination one finds out that both structures are in fact built from the same structural units upon different principles. This is apparent from Figure 1. The spectra nevertheless look different. One therefore cannot expect that the spectrum of realgar can be of great help in the interpretation of the spectrum of orpiment. Some points, however, are worth mentioning. Upon comparing the Raman spectrum of orpiment (Figure 3) with realgar, the absence for orpiment of very strong bands below 60 cm^{-1} is striking. The two strongest bands observed in this region for realgar were interpreted as deformations of the ring involving movement toward and away from each other of the arsenic atoms located in the same side of the plane of sulfurs. However, while in realgar the shortest As-As distance is 2.59 \AA , in orpiment, it is 3.25 \AA (Morimoto, 1954). Since this distance is of the order of the van der Waals diameter in arsenic, no sensible contribution from an As-As interaction is expected for orpiment. This could be the reason why no strong bands appear below 60 cm^{-1} in the Raman spectrum of orpiment.

Lu and Donohue (1944) examined orpiment by electron diffraction and found that, as a vapor, it consists of As_4S_6 molecules. They suggested that the crystal should be related to As_4S_6 molecules, in the same way that orthorhombic Sb_2O_3 is to Sb_4O_6 and, possibly, even as monoclinic As_2O_3 is to As_4O_6 . However, monoclinic As_2O_3 has not yet been analyzed spectroscopically, and no comparison of this sort is possible at present.

In the spectrum of orpiment also one can distinguish three distinct spectral regions where the strongest bands seem to assemble. The first, below 70 cm^{-1} , contains a few bands of medium and weak intensity which should be due to lattice vibrations. Between 100 and 200 cm^{-1} are bands due to S-As-S angle bending and from 300 to 400 cm^{-1} approximately, is the As-S stretching region. Table 2 shows that, for orpiment also, the less intense Raman bands are easily explained as overtones or combination tones.

CONCLUSIONS

The advantage of knowing the infrared absorption spectrum as well as the Raman spectrum of natural minerals for identification and analytical purposes is well known. We have tried to show here that the possibility of studying minerals by far infrared absorption and laser-excited Raman spectroscopy gives the opportunity of gathering essential information also for the knowledge of their structure. These techniques are especially useful for minerals containing heavier atoms, as was the case of realgar and orpiment presented in this paper. The preparation of the samples to

be investigated is extremely simple, requiring only that the mineral be ground to a powder. For Raman spectroscopy frequently no preparation is necessary.

Since minerals are generally insoluble, and melt only at high temperatures, it might be very difficult, or even impossible, to make a detailed interpretation of the observed vibrational spectra. This happened with orpiment. In other cases, as with realgar, when the molecular structure and the spectrum are simpler, a qualitative interpretation can be straightforward.

Additional help in establishing more reliable assignments in these cases could have come from the spectra of other minerals or compounds possessing an analogous structure. In our case the knowledge of the spectra of the AsS_4^{2-} ion and of the N_4S_4 molecule was useful. Possibly a still more useful analogy could have come from the appropriate arsenic oxides if their vibrational spectra were known.

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