Optics in India: The Spectroscopic Behavior of Rock Salt

C. V. Raman

The origin of the infrared activity of rock salt is discussed in terms of the free vibrations of the crystal. Experimental data on the Reststrahlen frequencies and on the frequency displacements of scattered radiation are used to explain the spectroscopic behavior of rock salt in the near infrared.

Rock salt was one of the first minerals of which the crystal structure was established by x-ray analysis. Its structure may be described in simple terms as made up of two interpenetrating lattices, each composed of atoms of one kind. The sodium atoms in one lattice are surrounded by six chlorine atoms in the other lattice and vice versa, in such manner that the grouping exhibits cubic symmetry. The sodium and chlorine atoms appear interspersed with each other in the cubic planes of the structure, while in the octahedral planes they appear separately in alternate layers.

The transparency of rock salt over a wide spectral range extending from 0.2 μ to 10 μ makes it a material of first-rate importance in applied optics and especially for use as dispersing prisms in the infrared. The dispersive power of rock salt is very low, between 1 μ and 5 μ, but improves at greater wavlengths. On the other hand, the absorption which is negligible at 10 μ becomes sensible at 13 μ and increases rapidly beyond 15 μ. Hence, rock salt may best be used as a prism material for infrared spectroscopy between 7 μ and 14 μ. It ceases to be useful beyond 15 μ.

It is well known that rock salt exhibits, in the region of long wavelengths, a high reflecting power which reaches its maximum value of about 90% at 54 μ. The strength of this reflection falls off rapidly at shorter wavelengths and is negligibly small for all wavelengths less than 33 μ. The fall is less rapid for wavelengths greater than 54 μ and the reflecting power reaches a limiting value of about 20% at 100 μ. These facts call for explanation; in particular, it may be

asked why, at 15 μ which is outside the spectral region of strong reflections, the absorbing power is nevertheless large enough to impair the usefulness of the material for infrared spectroscopy.

It is proposed in this paper to review briefly the contents of a memoir by the author which has been recently published and in which the spectroscopic behavior of rock salt has been discussed in detail.[1]

The Free Vibrations of the Structure

The dispersion, absorption, and reflection of infrared radiation by a crystal are effects arising from the interaction of the electromagnetic field in the radiation with the structural units composing the crystal. As a first step toward an understanding of these effects, it is necessary to consider the nature of the spectrum of the free or spontaneous vibrations of these structural units. We may deduce their modes and frequencies by the methods of classical mechanics. For this purpose, the atomic nuclei may be regarded as simple mass particles and the electronic clouds surrounding them as massless springs which hold the structure together. The relevant theory is fully set out in the memoir cited above and it is sufficient here to state the results to which it leads.

It emerges that the vibrational mode of highest frequency of the rock salt structure is one in which the atoms of sodium and chlorine oscillate against each other in opposite phases. Eight other modes of free vibration are also possible. They may be described simply in terms of the crystal structure: four of the modes are oscillations of the cubic layers, while the other four modes are oscillations of the octahedral layers, the movement alternating in phase from layer to layer, and being either normal or tangential to those layers. Since the oscillations of the sodium and

The author is the director of the Raman Research Institute, Bangalore, India.

chlorine atoms may be either in the same phase or in opposite phases, we have four modes for the cubic layers and four modes for the octahedral layers, and hence eight in all. The oscillations of the sodium and chlorine atoms located in the same cubic layers would be coupled with each other. But the oscillations of the sodium and chlorine atoms, appearing as distinct layers in the octahedral planes, would be independent.

The Origin of Infrared Activity

We next proceed to consider the relation between the free vibrations of the structure of the crystal and the effects arising from the passage of infrared radiation through it. The electric field in the incident radiation acts both on the positively charged nuclei and on the negatively charged electrons. But in all the modes of vibration with which we are concerned, there are as many positively charged nuclei moving in one phase as there are others moving in the opposite phase. It can be shown that, as a consequence, the displacements of positive charge when totaled up cancel out in all the modes under consideration. Hence, the free vibrations of the structure cannot be excited by the forces exerted by the field on the atomic nuclei. Necessarily, therefore, the movements of the atomic nuclei can have no effect on the radiation passing through the crystal. We conclude that the infrared activity of the crystal arises solely by reason of the forces exerted by the field on the negatively charged electrons and of the resulting movements; such activity is only possible when the displacements of negative charge produced do not cancel out when summed up over each structural unit.

Since the electrons are held in position by their interactions with each other and with the positively-charged nuclei, the displacements of negative charge induced by the field would necessarily disturb the nuclei from their positions of equilibrium. But the nuclear movements thus arising would not contribute to the infrared activity. Thus, while in the free vibrations of the structure, the massive, positively charged nuclei play the leading role and the electrons a subsidiary one, the situation is reversed in respect of the infrared activity, the electrons here playing the leading role and the nuclei a subsidiary one. In other words, the spectrum of free vibrations and the spectrum of infrared absorption are essentially different in their nature and origin. Both being properties of the same structure, we may expect to find some resemblances, but nothing in the nature of an identity or complete correspondence is to be expected.

The Reststrahlen Reflections

The considerations set forth above indicate that the mode of vibration in which the sodium and the chlorine atoms oscillate in opposite phases would be that exhibiting by far the strongest infrared activity. Their approach and recession would be accompanied by a periodic movement of the electronic cloud located between each pair of nuclei. The effects due to the displacements of electric charge in the successive cells of the structure would be additive and would thereby attain a large magnitude. Indeed, the activity may be expected to be so great that secondary radiations would emerge from the units of the structure along the external boundary of the crystal and conspire to give a powerful surface reflection. There would also be a strong absorption and extinction of the radiation actually penetrating into the crystal.

As a matter of actual observation, the surface reflection appears with great strength between 50 μ and 60 μ, its maximum of intensity being at 54 μ. On the other hand, the minimum of transmission by very thin films of rock salt appears at about 60 μ, being thus displaced a little further into the infrared. In what follows, we shall take 56 μ to be the wavelength corresponding to the frequency of the strongly active mode of free vibration of the rock salt structure.

Infrared Activity of Higher Orders

The absorption of infrared radiation arises when the electromagnetic energy of the field is taken up and transformed into vibrational energy in the crystal. When the frequencies of the field and the mechanical vibration are identical, a quantum of radiational energy changes over to a quantum of vibrational energy. There are also other possibilities: the energy of the radiation taken up by the crystal may appear as two, three, or a larger number of quanta of vibrational energy. Thus, we are led to expect, besides the intense absorption around 56 μ, a series of other absorptions around 28 μ, 19 μ, and 14 μ, respectively. They may be referred to as the absorptions of the second, third, and fourth orders, respectively. The possibility of observing the higher orders of absorption arises by reason of the first-order absorption being itself of great strength. The absorptions of higher order would necessarily be weaker and of progressively diminishing strength with increasing order. Nevertheless, when the absorption path is sufficiently increased, their effect on the transmission should be observable.

That the lack of transparency of rock salt at wavelengths greater than 15 μ, which renders it unusable as material for dispersing prisms, is due to these absorptions of higher order may be inferred from the observed facts of the case. The absorption at 14 μ is noticeable when the thickness of the plate is 5 cm or more, but it ceases to be significant when the absorption path is reduced to 3 cm or less. Yet in this range of thickness, there is a complete cutoff of the incident

radiation commencing at 19 μ and extending to greater wavelengths. Reducing the thickness to 15 mm produces but little observable change in this behavior, the wavelength of cutoff drifting slightly to 20 μ. Not until the thickness is reduced to 1 mm or so does the transmission at 19 μ become at all comparable with that observed at 14 μ with far larger thicknesses. To obtain such a free transmission at 28 μ, the path has to be further reduced to about 50 μ, while only films which are a few microns thick would give an observable transmission at 56 μ. It is evident from such facts that we are dealing with absorptions of altogether different orders of magnitude in these four cases.

The Infrared Activity of the Other Modes

We have now to consider the eight other modes of free vibration mentioned earlier. By reason of the vibrations being in opposite phases in the alternate layers, the displacements of electric charge in all the eight modes cancel out in the *first* approximation. But in the case of the four coupled oscillations of the sodium and chlorine atoms appearing in the cubic layers, the displacements of electric charge do not cancel out in the *second* approximation; there is a surviving component having twice the frequency of the mode under consideration. Hence these coupled vibrations would be strongly infrared active, but with doubled frequency in each case.

Taking 56 μ as the wavelength of maximum infrared activity, the wavelengths corresponding to the four modes referred to may be theoretically estimated to be 66 μ, 78 μ, 90 μ, and 108 μ, respectively. The halved wavelengths at which their second-order activity would manifest itself would therefore be 33 μ, 39 μ, 45 μ, and 54 μ, respectively.

The foregoing figures enable us to understand why the spectral region in which the strong surface reflections appear extends toward shorter wavelengths up to 33 μ and terminates at that wavelength. This extension is clearly the result of the superposition of the effects due to these modes and that of the mode of greatest activity. The activities of these modes appearing at 33 μ, 39 μ, 45 μ, and 54 μ are likewise responsible for the features noticeable in the spectral transmission curves of thin plates and thin films of rock salt at these wavelengths. These features have been observed and reported by Mentzel and by Barnes and Czerny in their studies on the infrared behavior of rock salt.

By reason of their symmetry properties, the vibrations of the sodium and chlorine atoms appearing in the layers parallel to the octahedral planes can exhibit no infrared activity. They, and indeed all the other modes as well, are accessible to observation by other spectroscopic methods. In this way, all the nine characteristic wavelengths of rock salt can be determined:

viz., 56 μ, 59 μ, 64 μ, 66 μ, 71 μ, 78 μ, 85 μ, 90 μ, and 108 μ. These wavelengths form a nearly continuous sequence extending into the region of great wavelengths far beyond that at which the maximum intensity of surface reflection appears. We are thereby enabled to understand why the spectral region, in which strong surface reflections appear, extends up to 100 μ. An intense excitation of the electrons in a thin layer adjacent to the surface of the crystal must of necessity involve all the nine possible modes of vibration and not only that of the mode of highest frequency. The strength of the excitation of any particular mode would be determined by the difference between its frequency and that of the most highly active mode. It would, therefore, fall off steadily as we recede from the mode having the highest activity towards lower frequencies and longer wavelengths.

The Spectrum of Light Scattering

The picture of the dynamical behavior of the rock salt structure and its relation to the infrared behavior of the crystal briefly summarized above finds a striking confirmation in the results of two other entirely independent lines of research. The first is the evaluation of the thermal energy of rock salt over the whole range of temperatures extending from absolute zero upwards, the theoretically determined and spectroscopically confirmed frequencies of vibration of the structure and their respective degeneracies being the basis of the calculation. To enter into this subject would take us beyond the field of applied optics; we shall therefore here only deal with the other line of investigation. This is a spectroscopic method closely related to the field of infrared studies, viz., the study of the spectral shifts observed in the scattering of monochromatic light in its passage through rock salt.

The frequency shifts observed in the scattering of light arise from the periodic changes in the optical scattering power of the structural units in the crystal. These changes are produced by their internal vibrations and hence the observed shifts may usually be identified with the frequencies of the vibrations. But in a particular class of cases, frequency shifts are recorded with notable intensity in the spectrum of the scattered light, which are double the frequency of the vibrations of the structure. The frequency shifts observed with rock salt are all of this kind, and the reason for this is not far to seek: In each of the nine modes of free vibration, we find a sodium atom approaching a chlorine atom on one side and simultaneously receding from a chlorine atom on the other side, and vice versa. The increased scattering power due to the approach is set off by the decrease due to the recession and cancels out in the *first* approximation. But in the *second* approximation, there is a residue left over, and this
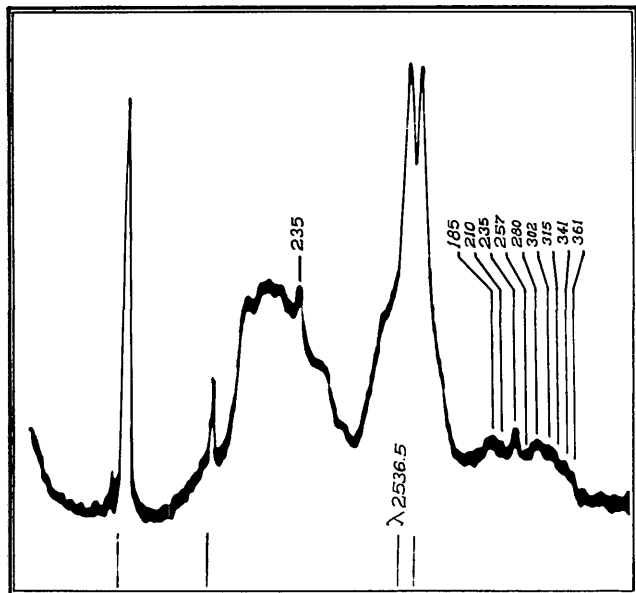
Fig. 1. Rasetti's microphotometer record of the rock salt spectrum.

would evidently be periodic but with a doubled frequency.

The spectrum of the scattering of light in rock salt was successfully recorded several years ago by Rasetti in a noteworthy investigation. The microphotometer record of the spectrum obtained by him is reproduced from his paper as Fig. 1. The frequency shifts in wavenumbers have been marked in the figure. The record shows the position of the exciting radiation (2536.5 Å) from a water-cooled mercury arc enclosed in quartz which was placed between the poles of an elec-

tromagnet in order to eliminate the self-reversal of the emitted radiation. The frequency shifts were both negative and positive, and they appeared respectively to the left and to the right of the position of the exciting radiation in the microphotometer trace.

The negative shifts are recorded with great intensity and, being overexposed in the original spectrogram, are not so clearly resolved from each other in its microphotometer trace as the positive shifts. These latter appear as successive steps in the record, and the respective frequency shifts are easily read off from their displacements with respect to the λ 2536.5 line. It will be seen that all the nine different frequency shifts may be clearly recognized. Their values as read off from the record on the right-hand side are in excellent agreement with the doubled frequencies of the respective modes, as theoretically estimated.

The relative intensities of the nine negative-frequency shifts as indicated by Rasetti's microphotometer record are also in satisfactory accord with the estimates based on the nature of the individual modes and their respective degeneracies. It should be mentioned the frequency shifts of ± 235 cm^{-1} stand out in Rasetti's original spectrogram as sharply defined lines. They represent the doubled frequency of vibration of the chlorine atoms located in the octahedral layers in which the movements are parallel to these layers. The notable intensity of the 235 cm^{-1} line is a consequence of the eightfold degeneracy of the mode.

Reference

1. C. V. Raman, Proc. Indian Acad. Sci. Sec. A **54**, 253–304 (1961).

Meetings Calendar

31–
June 7　International Television Conference, London *In-stitution of Electrical Engineers, Savoy Place, London, W.C.2, England*

late　Interphoto Congress, Copenhagen *International Photography and Cinematography Dealers Association, Steienvorstadt 63, Basel 10, Switzerland*

late　Washington Symposium on Use of Artificial Satellites for Geodetic Purposes *International Association of Geodesy. 18 rue Auber, Paris IX. France*

late　Journées de la Lumière, Grenoble *W. Bing, Assoc. Francaise de la Lumière, 4 rue Ed.-Rousse, Paris 14e, France*

June

4–8　French Soc. of Physical Chemistry, Paris *Secrétaire Général, Société de Chimie Physique, 10 rue Vauquelin, Paris 5e, France*

5–8　24ème Congrès Annual du GAMS *Secretariat, 1 rue G. Boissier, Paris XV, France*

7–10　Canadian Association of Physicists 17th Annual Congress, Hamilton, Ontario,

11–14　Instrument Society of America, Seattle, Wash., Instrument-Automation Conference and Exhibit *W. H. Kushnick, 313 6th Ave., Pittsburgh 22, Pa.*

11–15　Columbus Symposium on Molecular Structure and Spectroscopy *R. A. Oetjen, Dept. Physics, Ohio State University, Columbus 10, Ohio*

18–22　Eindhoven Congress on Magnetic and Electric Resonance and Relaxation *D. J. Kroon, Natuurkundig Laboratorium, N.V. Philips' Gloelampenfabriek, Eindhoven, Netherlands*

18–22　International Conference on Spectroscopy, Univ. of Maryland *B. F. Scribner, National Bureau of Standards, Washington 25, D.C.*

19–21　APS Summer East Mtg., Evanston, Ill. *K. K. Darrow, Columbia Univ., New York 27, N.Y.*

24–29　ASTM National Meeting and Apparatus Exhibit, Statler Hotel, New York *ASTM, 1916 Race St., Philadelphia 3, Pa.*

25–29　Institute of Nuclear Magnetic Resonance, Buffalo *H. A. Szymanski, Chemistry, Canisius College, Buffalo 8, N.Y.*

25–30　Copenhagen Symposium on Electromagnetic Theory and Antennas *H. Lottrup Knudsen, Oster Voldgade 10 G, Copenhagen K, Denmark*

July

—　Munich Symposium on Crystallographic Computing *D. W. Smits, International Union of Crystallography, c/o Mathematisch Institut., Univ. of Groningen, Reitdiepskade 4, Groningen, Netherlands*

8–14　6th International Commission on Glass, Washington, D.C. *C. H. Hahner, General National Committee, c/o Glass Section, National Bureau of Standards, Washington D.C.*

9–11　11th International Astrophysics Symposium, Liège *P. Swings. Inst. of Astrophysics, Sciessin, Belgium*

9–20　Summer Course in Optics *Inst. of Optics, River Campus Station, Rochester 20, N.Y.*

10–20　Summer Course on Techniques of Infrared Spectroscopy *Director, Center for Continuation Study, Univ. of Minn., Minneapolis 14, Minn.*

16–19　International Colloquium on Novae, Novoids and Supernovae, Lyons *J. Dufay, U. de Lyons, rue de Cavenne, Lyons, France*

16–20　IUPAP Conference on Paramagnetic Resonance, Jerusalem *W. Low, Hebrew Univ., Jerusalem, Israel*

16–20　International Conference on the Physics of Semiconductors, Exeter. *IPPS, 47 Belgrave Square, London, S.W.1, England*

25–31　Symposium in Commemoration of Fiftieth Anniversary of the Discovery of X-Ray Diffraction and of Crystal-structure Analysis, Munich *F. Bopp, Inst. für Theoretische Physik, Schellingstr. 4–8, Munich, Germany*

August

—　3rd International IUPAP Symposium on X-ray. Microscopy and X-ray Microanalysis, Stanford *H. M. Pattee, Dept. Physics, Stanford Univ., Stanford, Calif.*

5–11　2nd International Congress on Radiation Research, Harrogate *A. Howard, Mount Vernon Hospital, Northwood, Middlesex, England*

6–10　Society of Photographic and Instrumentation Engineers Meeting, Biltmore Hotel, New York.

6–17　MIT Infrared Summer Course *J. M. Austin 7-103, MIT, Cambridge 39, Mass.*

13–15　Interdisciplinary Conference on Electromagnetic Scattering, Potsdam, N.Y. *M. Kerker, Clarkson College of Technology, Potsdam, N.Y.*

14–16　Boulder International Conference on Precision Electromagnetic Measurements *G. Birnbaum, Hughes Research Lab., Malibu, Calif.*

14–18　Fisk Infrared Summer Course *Director, Fisk Infrared Institute, Fisk Univ., Nashville, Tenn.*

19–26　Sixth General Assembly of International Commission for Optics and Congress on Image Formation, Munich *H. Schober, Institut für Medizinische Optik, Arnulstr. 205, Munich, Germany*

21–24　International Symposium of Far Infrared Spectroscopy, Sheraton-Gibson Hotel, Cincinnati *F. F. Bentley, ASD, Wright Patterson AFB, Ohio*

21–28　Copenhagen International Congress on Acoustics *F. H. B. Interslav, Tekniske Hojskole, Ostervoldgade 10, Copenhagen, Denmark*

27–29　7th Symp. Ballistic Missile and Space Technology *Aerospace Corp., P.O. Box 95085, Los Angeles 45, Calif.*

27–29　APS Summer West Mtg., Seattle, Wash. *H. A. Shugart, Physics, Univ. of Calif., Berkeley 4, Calif.*

27–30　American Astronomical Society Meeting, Yale Univ. *H. Smith, Yale U. Observatory, New Haven, Conn.*

27–31　Infrared Gordon Conference, Meriden, N.H.

27–
Sept. 1　2nd International Conference on Information Processing, Munich *IFIPS, 1634 Arch St., Philadelphia 3, Pa.*

30–Sept. 5　Symposium on Photo Interpretation, Delft *Commission VII Intl. Training Centre for Aerial Survey, Kanaalweg 3, Delft, Netherlands*

September

—　British Assoc. Advancement Science Int'l Meeting, Manchester *G. Allen, Burlington House, London, W. 1, England*

3–7　Brussels International Symposium on Information Theory *F. L. Stumpers, Philips Research Labs, Eindhoven, Netherlands*

5–7　Emittance and Reflection of Radiation from Various Materials and Space Applications *Univ. of Dayton*

7–12　Kyoto International Conference on Crystal Lattice Defects *R. R. Hasiguti, Univ. Tokyo, Bunkyoku, Tokyo, Japan*

9–14　Dallas Technical Conference of the Illuminating Engineering Society

10–15　IUPAC Tokyo International Symposium on Molecular Structure and Spectroscopy *Science Council of Japan, Ueno Park, Tokyo, Japan*

16–20　Electrochemical Society Meeting, Statler Hilton Hotel, Boston, Mass.

17–19　9th Ottawa Symposium on Applied Spectroscopy *B. Farrar, J. T. Donald & Co. Ltd., 1181 Guy St., Montreal 25, Que., Canada.*

17–22　6th Intl. Congress on High Speed Photography, Scheveningen *J. G. A. de Graaf, 14, Burgemeester de Monchyplein, The Hague, Netherlands*

24–28　Union of German Physical Societies, Stuttgart *H. Franke, Verband Deutscher Physik. Gesell., Gänseheide 15A, Stuttgart, Germany*

October

—　Infrared Information Symposium Fall Meeting Eastern States

—　URSI Montreal Meeting *M. G. George, Thayer School of Engineering, Dartmouth College, Hanover, N.H.*

—　Varian Annual NMR-EPR Workshop *Varian Assoc., Hansen Way, Palo Alto, Calif.*

4–6　**Optical Society of America 47th Annual Meeting, Manger Hotel, Rochester** *Hilda Kingslake, 56 Westland Ave., Rochester, N.Y.*

5　**OSA Annual Business Meeting,** *Manger Hotel, Rochester, N.Y.*

15–19　Instrument Society of America 17th Annual Instrument-Automation Conference and Exhibit *W. H. Kushnick, 313 6th Ave., Pittsburgh 22, Pa.*