Vibrational Spectra of MnO₄⁻ Isolated in KBr Crystals
An Illustration of Pure $T_d$ Symmetry in the Solid State

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In introductory lectures of group theory in vibrational spectroscopy, carbon tetrachloride is commonly used as an example of a tetrahedral molecule (1). However, the polarization of the Raman lines are subject to motional averaging (2), which complicates a straightforward demonstration of the symmetry properties of the molecule. We felt the need for a solid state example which can clearly illustrate the rigorous application of IR and Raman selection rules in a pure $T_d$ symmetry.

In this note, we present the vibrational spectra of MnO₄⁻ matrix isolated in KBr. MnO₄⁻ ion has been subject to several spectroscopic studies earlier (3–5) both in solutions and in different crystalline environments. The choice of this particular system is based on the following criteria: (1) Single crystals of KBr doped with MnO₄⁻ can easily be grown with the glassware available in any chemistry laboratory (see experimental section). The crystals are stable under normal conditions and can be handled without any special care. (2) The host matrix KBr, which is often used to make pellets for IR spectra, does not absorb in the spectral domain of MnO₄⁻ ion. (3) Unlike the other $T_d$ molecules, there is little Fermi resonance interference. (4) The orientation of the crystals is straightforward since they grow in the form of cubes with natural (100) faces. The MnO₄⁻ ion substitutes for a Br⁻ anion and as shown in Figure 1, the macroscopic crystal axes can thus be directly used (without cutting) as the referential axes for the polarized Raman measurements. (5) Finally, the first electronic band of charge transfer character of MnO₄⁻

Figure 1. Schematic representation of the Raman experiment (spectrometer with 90° configuration) described in the text. The figure depicts the laboratory axes and the polarization geometries used. Also shown is the structure of the KBr:MnO₄⁻ crystal. The Raman tensor elements are expressed as, for example, $z(x,y)$, where $z = \text{direction of incidence}$ and $y = \text{direction of observation}$. The polarizability tensor component is $(x,y) = \alpha_{xy}$.

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lies around 510 nm. Thus the Raman intensities of the very
diluted MnO₄⁻ are greatly enhanced through a resonant
Raman effect (5) when one uses the visible exciting lines of
the Argon ion laser (614.5 and 488 nm).

Theory
Raman effect occurs because of a change in magnitude or
direction of the electronic polarizability during the
doctoral motion, while infrared absorption occurs because of a
change in magnitude or direction of the electric dipole mo-
dment during the motion. The magnitude of the induced
dipole moment $P$ is given by

$$|P| = |\alpha E|$$  \hspace{1cm} (1)

where $E$ is the electric vector of the incident radiation of
frequency $\nu$ and $\alpha$ the polarizability. If $\alpha$ changes during the
vibration $i$ with frequency $\nu_i$, $P$ will change with the frequen-
cies $\nu + \nu_i$ and $\nu - \nu_i$ as well as with frequency $\nu$. The scattered
light will thus contain the frequencies $\nu \pm \nu_i$ in addition to $\nu$.
Therefore, the Raman record is obtained by spectral analy-
sis of the light scattered from the sample illuminated by a
laser source (Fig. 1); it has the form of the intensity $I$ of the
scattered light versus the displacement of the frequency
from the incident laser frequency. Each Raman vibrational
band is characterized by its frequency, intensity, linewidt,
and depolarization ratio. The first three parameters are
obtained directly from the experimental spectra. To measure the
depolarization ratio, one has to record the spectra with the
analyzer parallel and perpendicular, respectively, to the
incident electric field vector. This means, for instance, that
when the incident electric field ($E_{in}$) is parallel to $P_o$ one has to
record spectra with the analyzer parallel to $P_{xx}$ ($I_{xx}$ =
intensity of the given line) and $P_{xy}$ ($I_{xy}$ = intensity of the same line).
The ratio ($I_{xx}/I_{xy}$) is the depolarization ratio.

When the sample is a single crystal, it is possible to choose
such orientations of the sample axes with respect to the inci-
dent beam so as to measure individual elements of the polariz-
ability tensor. Group theory relates the point symmetry of
the molecule. Further, in normal Raman spectroscopy (NRS), the exci-
ting frequency lies in the region where the molecule has no
electronic absorption band while in resonant Raman spec-
troscopy (RRS), it falls within the electronic band. Thus, in
NRS, the Raman intensity is relatively independent of the
exciting frequency while in RRS there may be an enhance-
ment of the Raman lines. It follows, therefore, that MnO₄⁻
which has an electronic band around 510 nm (9) is indeed
subject to a RRS. Several articles in this Journal (10, 11)
have treated the subject of RRS.

Results and Analysis
Figure 2 shows a survey Raman spectrum of MnO₄⁻ in a
KBr crystal at room temperature. The infrared spectrum
shows a single sharp absorption line at 926 cm⁻¹. The four
normal modes expected in a tetrahedral XY₄ molecule trans-
form as $A_1$, $E$, $2T_2$, respectively. Inspection of the charac-
ter table of the $T_d$ group shows that only the modes transform-
ning as $T_2$ are IR and Raman active. Therefore, the line at 927
$	ext{cm}^{-1}$ transforms as $T_2$ since it is observed in both IR and

$$[\alpha_{rr}]^m = \int \alpha_{rr} \psi_{m} \psi_{n} \, dr$$

are the matrix elements of the six components of the polariz-
ability tensor. The diagonal matrix elements ($n = m$) of $\alpha$ or
$P_o$ correspond to Rayleigh scattering, whereas the off-diagonal
elements (i.e., transitions $n \neq m$ induced by the incident
light wave) correspond to Raman scattering. Thus, from eq.
5, a Raman transition $n \neq m$ is allowed if at least one of the
six quantities $[\alpha_{rr}]^m$, $[\alpha_{rr}]^m$, ... is different from zero. If we
now consider the vibrational Raman spectrum, $\psi_m$ and $\psi_n$
will be the vibrational eigenfunctions $\psi_m$ and $\psi_n$ of the upper
and lower states. Then, a Raman transition is allowed be-
tween two vibrational levels $v'$ and $v''$ only when at least one of
the six products $\alpha_{rr} \psi_m \psi_n$, $\alpha_{rr} \psi_m \psi_n$, etc., is totally
symmetric, that is, remains unchanged for all the symmetry
operations pertaining to the molecule. This will happen only
when the product $\psi_m \psi_n$ has the same species as at least one of
the six components $\alpha_{rr}$, $\alpha_{rr}$ ... of the polarizability tensor.
Thus we see that there is a direct relationship between the
Raman intensity and the symmetry properties of the
molecule.

Figure 2. Unpolarized survey Raman spectrum of MnO₄⁻ doped in a KBr crystal
at room temperature. $\lambda_{exc} = 514.5$ nm. Laser power on the crystal = 0.23 W.
Spectral resolution = 5 cm⁻¹. The inset presents an expanded spectrum in the
region 770–890 cm⁻¹, which clearly shows the two weak lines at 813 and 832
$	ext{cm}^{-1}$.
Raman spectra. Polarized Raman spectra (Fig. 3) confirm this assignment. Indeed the nondiagonal elements of the Raman tensor XY, YZ, and XZ transform as T2 according to the character table. The Raman line observed at 407 cm⁻¹ has the same polarization behavior as the line at 927 cm⁻¹. This T2 mode should, in principle, be seen in the IR spectra also (12). But owing to the low concentration of MnO₄⁻ in KBr crystals, the line at 407 cm⁻¹ does not show up clearly in the IR spectra. The two remaining bands at 367 and 848 cm⁻¹ observed in the Z(XX)Y polarization pertain to E or A₁ geometry according to group theory (examine the Tₐ group table in conjunction with Fig. 3).

The precise assignments of the observed transitions is obtained by an additional Raman measurement. Using the 514.5 nm line of the Argon ion laser, the resonant Raman spectrum of MnO₄⁻ in KBr reveals two intense band progressions, namely 848, 2 X 848, 3 X 848 cm⁻¹, etc., and 927, 927 + 848, 927 + 2 X 848 cm⁻¹, etc. In resonant Raman spectra, it is common to observe harmonic progressions of the totally symmetric mode (I₀). The 848 cm⁻¹ line is thus assigned to the totally symmetric mode (ν₁) and, accordingly, the line at 367 cm⁻¹ to the E mode (ν₃). As the force constants of stretching modes are qualitatively expected to be stronger than those of bending modes, the T₂ mode at 927 cm⁻¹ may be assigned to ν₃ and the other at 407 cm⁻¹ to ν₄, where we use the notation followed by Nakamoto (2).

A careful inspection of the Raman spectrum shows two additional very weak lines at 813 and 832 cm⁻¹ (inset in Fig. 1). One of them at 832 cm⁻¹ likely arises on the crystal the A₁ mode of MnO₄⁻ containing one oxygen-18 ion. Strictly speaking, this molecule has trigonal symmetry (C₃ᵥ). But, it is known (1) that at this level of analysis the molecule can still be assumed to be cubic. Then, as this mode is nondegenerate, a simple model calculation is appropriate. It relates the frequencies pertaining to the two species: MnO₄⁻ with four O¹⁸ and MnO₄⁻ with three O¹⁸ and one O¹⁶. Indeed, the frequency ratio 18/16 is proportional to

\[
\left( \frac{\text{four times the mass of }^{18}O}{\text{three times the mass of }^{16}O + \text{mass of one }^{18}O} \right)
\]

Applying this factor to the 848 cm⁻¹ line, one calculates the frequency to be about 835 cm⁻¹. Experimentally one observes 832 cm⁻¹. A second argument in favor of this identification is based on their intensities. Indeed, the relative intensity of the 832 cm⁻¹ line is approximately 0.7% while 0.8% would be expected considering the natural abundance of ¹⁸O (0.2%). The other line at 813 cm⁻¹ corresponds to the first harmonic of ν₂ at 407 cm⁻¹ within the experimental error in frequency reading of about 0.5 cm⁻¹.

Finally, in the foregoing discussion, we have assumed that all the MnO₄⁻ ions in the crystal are orientated in the same manner. This assumption seems valid in the present case because the polarization results clearly show the 100% extinction of A₁ and E lines in the (zxy) geometry and 2T₂ lines in the (zxy) geometry. In other words, any reorientational process of MnO₄⁻ ions is probably not within the time scale of a Raman measurement. This point has been discussed in more detail in ref 5. If the symmetry of MnO₄⁻ (with four O¹⁸ atoms) is postulated to be lower than Tₐ, one would expect to observe splittings of the degenerate E and T₂ modes. Figure 2 shows that all the four observed modes have approximately the same linewidth, and measurements at high resolution and low temperatures reveal no splitting. Additionally, we observe no breakdown of the selection rules. Thus, the pure T₂ symmetry of MnO₄⁻ is established.

**Experimental**

Single crystals of KBr doped with MnO₄⁻ have been grown by slow evaporation of aqueous solutions at room temperature. Pro analysis grade KBr and KMnO₄ powders were used. The solution contains typically 0.5% by weight of KMnO₄ with respect to KBr. Transparent and homogeneously colored crystals were selected for the measurements. The concentration of MnO₄⁻ incorporated in the crystals is estimated to be less than 0.05 mol %.

All the spectra have been obtained at room temperature. IR spectra were recorded using a Perkin-Elmer 597 spectrometer with crystals of about 2–4 mm thickness. Raman spectra have been obtained with our laboratory-assembled Raman spectrometer (Fig. 1) consisting of a Spectra Physics argon ion laser, a Spex monochromator, and a photon-counting system. The power on the crystal never exceeded 0.3 W, and the crystals showed no damage due to laser irradiation. The resonant Raman effect of MnO₄⁻ in KBr causes relatively different enhancements of the internal modes depending on the exciting laser line. We found that the 514.5 nm exciting line is the best suited for this experiment, because the E mode is not easily observed using other exciting lines owing to its weak intensity.

We would be pleased to provide copies of the original spectra to those not having a Raman spectrometer.

**Literature Cited**