

PHOTOINDUCED INSTABILITY OF MnO_4^- MOLECULAR DEFECTS IN POTASSIUM IODIDE

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Abstract. An instability of the MnO_4^- molecular ion in KI is reported that occurs under intense resonant excitation in the ${}^1A_1 \rightarrow {}^1T_2$ optical transition of the impurity. The intensities of resonantly excited vibrational Raman lines and the absorption strength have been used to monitor the time dependence of the effect which is investigated for different temperatures and excitation powers. A physical model is discussed that involves ionization of the molecular ion and qualitatively accounts for the experimental observations.

Key words: photochromic reaction, electronic states (localized), resonance Raman scattering.

1. INTRODUCTION

MnO_4^- belongs to a class of molecular ions with a tetrahedral (T_d) symmetry that are easily doped into potassium and rubidium halides, other examples being ReO_4^- , BF_4^- or ClO_4^- (see, e.g. [1–4]). The interest in these systems arises from the possibility of investigating in detail the impurity-induced changes in the optical and vibrational properties of the matrix as well as of the electron-vibrational and electron-lattice coupling. As is known from infrared and Raman spectra, molecular ions retain their symmetry when incorporated into the crystal lattice [5]. As they substitute the halide ion, it means in the case of MnO_4^- that the Mn–O bonds must be oriented along four of the possible eight $\langle 111 \rangle$ directions. This results in two equivalent orientations of the molecular impurity in the lattice, which are related by a $\pi/2$ -rotation about a $\langle 100 \rangle$ -type crystal axis.

The most obvious effect of the dopant on the optical spectrum is the occurrence of an additional absorption. In $\text{KI}:\text{MnO}_4^-$, the most prominent

band in the visible corresponds to a dipole-allowed ${}^1A_1 \rightarrow {}^1T_2$ impurity transition which, at low temperature, consists of a zero-vibrational ($N = 0$) maximum and up to $N = 5$ vibronic maxima. These reflect a strong coupling to the totally symmetric ν_1 (A_1) molecular vibration, while the width of each vibronic component is presumably due to lattice-phonon interaction. The Raman scattering resonantly excited in this absorption has provided detailed information on these interactions and has led to a thorough understanding of the local dynamics around the defect and the mechanisms of the vibronic interaction [5-8].

In this paper we report the discovery of an interesting instability of the MnO_4^- molecular ion in KI under resonant laser excitation in the ${}^1A_1 \rightarrow {}^1T_2$ optical transition. By using the intensities of the impurity-related Raman lines and the optical absorption strength as a probe, a time-dependent bleaching is observed which suggests a reduction in the centre concentration. Trying to reveal the possible origin of this effect, we have measured the temperature and the power dependence of the bleaching and we discuss a physical model that could explain our observation.

2. EXPERIMENTAL

The samples were cleaved from Czochralski-grown KI crystals doped by adding KMnO_4 to the melt. The MnO_4^- was then produced by applying an electric field by using the technique described previously [8].

For the measurement we used a standard spectroscopic equipment including an Ar^+ laser-pumped dye laser system tunable over most of the MnO_4^- absorption, a double monochromator, and photon counting electronics for signal detection. The sample temperature could be varied between 5 and 300 K. The Raman data were taken in 90° scattering geometry with the incident and scattered light propagating along [001] and [100], respectively. The polarization of the incident light was directed along [010], while the scattered light was unpolarized. A scrambler was inserted in front of the spectrometer to circumvent the polarization characteristics of our gratings so that truly unpolarized spectra were obtained.

The absorption spectrum was measured conventionally, except in the bleaching experiments. In these, a tunable dye laser (without monochromator) was used and the absorption was determined from the (relative) light intensity transmitted through the sample and detected by a photoiodide behind it. Although the dye laser could be scanned but over a limited spectral range without changing the dye, the virtue of this method is simplicity, as the laser beam, which at a higher power simultaneously induces bleaching, actually probes the bleached crystal volume.

In both the Raman and the absorption measurements, the laser was focussed into the sample by an achromatic $f = 250$ mm lens to produce a sufficiently high power density (of order 200 W/cm^2). In all bleaching

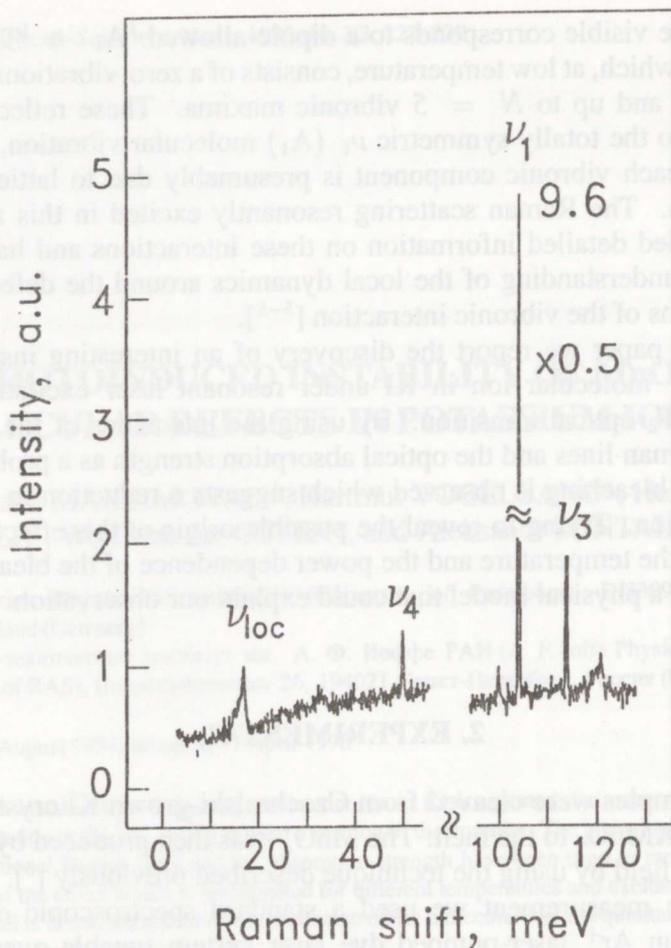


Fig. 1. Unpolarized first-order resonant Raman spectrum of KI:MnO_4^- at 5 K excited at $E_L = 2.4093$ eV, showing intramolecular and localized vibrations. The weak structures at 32.5, 99.9, and 120.8 meV (not labelled) are due to higher-order scattering processes ($2\nu_{loc}$, $2\nu_4$, $\nu_1 + \nu_{loc}$).

experiments, for each run either a new spot at the sample was selected or the sample was given sufficient time to recover at room temperature.

3. EXPERIMENTAL RESULTS

Figure 1 shows a low-temperature (5 K) Raman spectrum resonantly excited in the MnO_4^- $N = 3$ vibronic absorption with the 514 nm Ar^+ laser line ($E_L = 2.4093$ eV). As the second-order lattice phonon scattering [9] dominating at room temperature is largely reduced at 5 K, the features seen are essentially due to first-order processes involving the intramolecular vibrations of the MnO_4^- ion. Based on the polarization behaviour [3], the most intense line with the Raman shift of 103.1 meV (831.6 cm^{-1}) is attributed to the totally symmetric vibration ν_1 (A_1), while the weaker lines

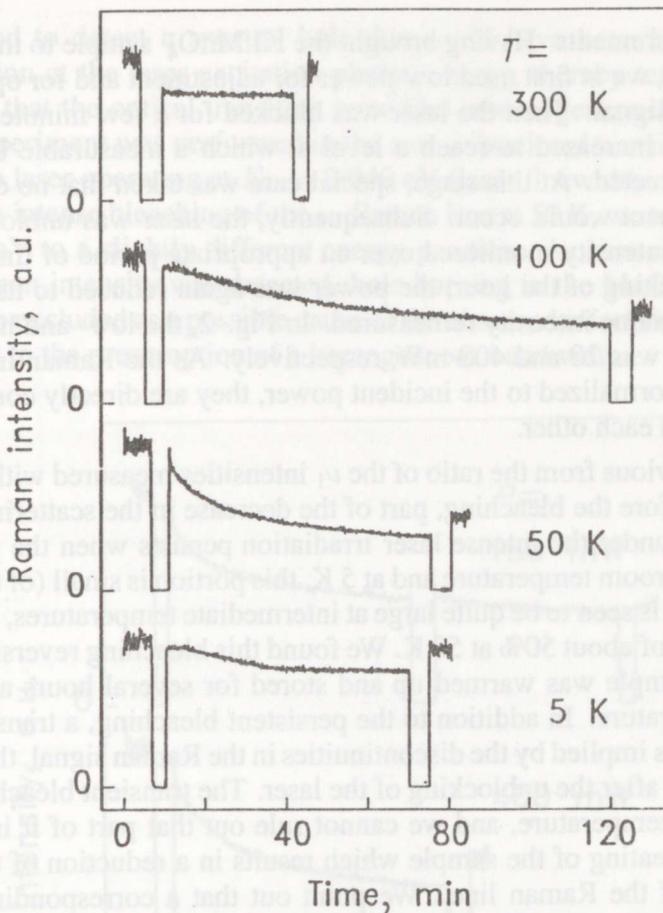


Fig. 2. Time dependence of the ν_1 Raman scattering intensity at different temperatures. The excitation photon energy $E_L = 2.4093$ eV. The excitation power was 20 mW before and after bleaching and 400 mW during bleaching. All intensities are normalized to the incident laser power (see the text).

at 113.9 meV (918.7 cm^{-1}) and 49.9 meV (402.5 cm^{-1}) are due to the triply degenerate vibrations ν_3 (F_2) and ν_4 (F_2), respectively. Well above the 1LO frequency of KI [10], a new local mode at 16.4 meV (132.3 cm^{-1}) as well as a higher-order scattering with relative intensities strongly varying with the excitation phonon energy (not shown) can be observed.

A striking new feature concerning these Raman transitions is the bleaching of the line intensity under laser excitation, whereby the strength and the time behaviour of the reduction depend on the sample temperature and the laser power. To study these effects we used a single laser with the power kept constant and monitored the resonantly excited Raman transitions either by measuring after bleaching the entire Raman spectrum or by directly following the peak intensity of a selected Raman line as a function of time.

Figure 2 illustrates the time dependence of the strong ν_1 line intensity at various temperatures and simultaneously explains the scheme employed

in the measurements. Having brought the $\text{KI}:\text{MnO}_4^-$ sample to the desired temperature, we at first used low power for adjustment and for optimizing the Raman signal. Then the laser was blocked for a few minutes and the laser power increased to reach a level at which a measurable bleaching could be detected. At this stage, special care was taken that no change in laser alignment would occur. Subsequently, the laser was unblocked and the Raman intensity monitored over an appropriate period of time. After another blocking of the laser, the power was again reduced to its original level and the line intensity remeasured. In Fig. 2, the low- and high-level laser power was 20 and 400 mW, respectively. As the Raman intensities shown are normalized to the incident power, they are directly comparable relative with each other.

As is obvious from the ratio of the ν_1 intensities measured with 20 mW after and before the bleaching, part of the decrease in the scattering signal that occurs under the intense laser irradiation persists when the power is reduced. At room temperature and at 5 K, this portion is small (of the order of 5%) but it is seen to be quite large at intermediate temperatures, reaching a maximum of about 50% at 50 K. We found this bleaching reversible only when the sample was warmed up and stored for several hours at around room temperature. In addition to the persistent bleaching, a transient one takes place as implied by the discontinuities in the Raman signal, that occur immediately after the unblocking of the laser. The transient bleaching also depends on temperature, and we cannot rule out that part of it is caused by a slight heating of the sample which results in a reduction of the peak intensities of the Raman line. We point out that a corresponding time-dependent persistent and transient bleaching was found for all other Raman lines (ν_3, ν_4, ν_{loc}) as well as for bleaching at different laser photon energies E_L . No bleaching at all could be discovered in MnO_4^- -doped KCl and KBr.

A very similar time behaviour of the Raman intensities resulted for different laser powers (Fig. 3). As optimum temperature in these experiments $T = 50$ K was chosen and the bleaching power varied between $P = 50$ and 800 mW. The low-power level for the adjustments was 20 mW in all cases. As is apparent from the figure, the increase in the laser power strongly affects the decay at short times, implying an appreciable transient bleaching. This becomes especially clear from the 800 mW data in which the Raman signal, after unblocking the laser, falls rapidly (i.e. within seconds) by about 30%. In this situation, the time response of our detection system seemed to be not fast enough to allow the signal return to its initial level. A closer inspection of the curves at longer times reveals that the decay rate slightly increases with power, but no saturation is reached after hours even at 800 mW. From the signals measured with 20 mW excitation a persistent bleaching can be estimated. It amounts to about 64% at 800 mW and is found to sublinearly increase with the excitation power, although more accurate measurements are needed to establish its exact functional dependence.

To clarify the origin of the observed change in Raman intensities, we

first tried to detect a spectral hole that could have been burnt into the absorption at the laser excitation photon energy, thereby tentatively presuming that the optical transition would be inhomogeneously broadened. This experiment was performed in the zero-vibrational transition ($N = 0$) with the laser operating at $E_L = 2.040$ eV (laser linewidth ~ 0.15 meV). After an intense bleaching of the ν_1 Raman line at 50 K, we tuned the laser by 1 meV to a slightly different energy position. As here no increase in the Raman intensity was detected, hole burning in the MnO_4^- absorption could be excluded as a possible cause of the observed effect simultaneously keeping to the presumption of a homogeneous bandwidth.

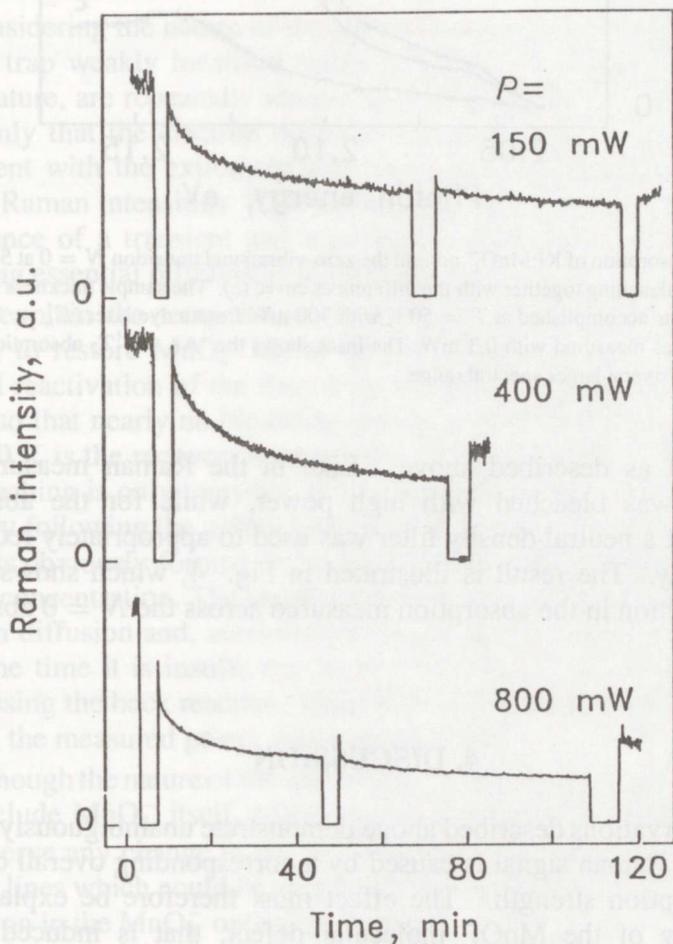


Fig. 3. Time dependence of the ν_1 Raman scattering intensity at different bleaching powers. $T = 50$ K. The intensities are normalized to the incident power which was 20 mW before and after bleaching and otherwise as indicated.

We therefore, in another experiment, carefully measured the absorption before and after bleaching over a larger spectral range. To have a sufficiently high bleaching intensity available and to guarantee that the transmission be actually probing the bleached part of the sample volume, we again used a single dye laser for both the bleaching and the absorption

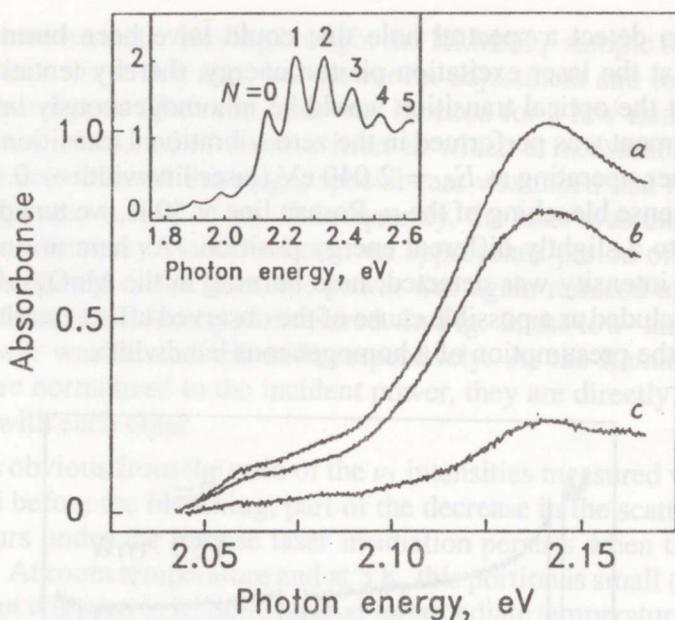


Fig. 4. Optical absorption of KI:MnO_4^- around the zero-vibrational transition $N = 0$ at 50 K before (a) and after (b) bleaching together with the differences curve (c). The sample thickness is 2.5 mm. The bleaching was accomplished at $T = 50$ K with 300 mW from a dye laser ($E_L = 2.040$ eV), the absorption was measured with 0.3 mW. The inset shows the ${}^1A_1 \rightarrow {}^1T_2$ absorption band of KI:MnO_4^- at 5 K over a larger spectral range.

measurement as described above. Like in the Raman measurements, the sample was bleached with high power, while for the absorption measurement a neutral density filter was used to appropriately reduce the light intensity. The result is illustrated in Fig. 4, which shows a clear overall reduction in the absorption measured across the $N = 0$ absorption component.

4. DISCUSSION

The observations described above demonstrate unambiguously that the decay in the Raman signal is caused by a corresponding overall decrease in the absorption strength. The effect must therefore be explained by an instability of the MnO_4^- molecular defect, that is induced by the optical excitation and that diminishes the defect concentration. At present, however, the physical model of the process is not very clear. Although likely at first sight, we definitely rule out the reorientation of the excited impurity molecule during vibrational deexcitation as found from high-resolution infrared hole burning for ReO_4^- in KI and RbI [2]. This process presumes that the configurational degeneracy of the molecular defect described above is removed by elastic strain gradients due to nearby defects resulting in a slight difference of the infrared absorption frequency for the two defect orientations. In the broad electronic absorption as well as in the

Raman line this would not give rise to any measurable change under optical excitation.

As a conceivable mechanism, we will consider the disintegration of optically excited MnO_4^- ions into neutral MnO_4^0 plus a free electron which subsequently becomes trapped. Since here the conduction band is involved which, compared to other potassium halides, in the iodides lies lower in energy by about 1 eV or more, it would qualitatively explain why the bleaching is restricted to KI (another possible material is RbI). Unfortunately, nothing is known about the optical and Raman transitions on MnO_4^0 which in this case are expected to grow and should allow to test this model.

Considering the nature of the electron trap, we believe that along with a deep trap weakly localized states are important which, depending on temperature, are repeatedly ionized until the electron is finally stabilized. Note only that the electron diffusion connected with this mechanism is consistent with the extremely slow and nonexponential decay observed for the Raman intensities. This mechanism also basically agrees with the occurrence of a transient and a persistent contribution of the bleaching revealing essential differences in the trap depth.

To explain the temperature dependence (Fig. 2) the back reaction tending to restore MnO_4^- has to be considered. At room temperature, thermal reactivation of the deep trap suffices to prevent the formation of MnO_4^0 so that nearly no bleaching occurs under resonant excitation (note that 300 K is the recovery temperature of our samples). Instead, most of the bleaching is only transient, as is clearly reflected by the rapid drop of intensity following the unblocking of the laser. By contrast, at $T = 50$ K, MnO_4^0 is obviously formed, as is seen from the persistent reduction of the MnO_4^- concentration. The smaller thermal energy thereby slows down the electron diffusion and, accordingly, the decay of Raman intensity, but at the same time it is insufficient to free the deeply trapped electron, thus suppressing the back reaction. Quite naturally this mechanism would also explain the measured power dependence (Fig. 3).

Although the nature of the electron trap remains unknown, we definitely can exclude MnO_4^- itself, which would transform into MnO_4^{2-} . We did not observe any change in the well-known MnO_4^{2-} absorption band or in Raman lines which could be ascribed to the formation of this defect under excitation in the MnO_4^- optical absorption.

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MnO₄⁻ MOLEKULAARDEFEKTIDE FOTOINDUTSEERITUD EBASTABIILSUS KAALIUMJODIIDIS

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On vaadeldud kaaliumjodiidi kristallis intensiivse resonantsergastuse mõjul lisandi optilises siirdes ${}^1A_1 \rightarrow {}^1T_2$ tekkinud MnO₄⁻ molekulaariooni ebastabiilsust. Selle efekti aegsõltuvuse ilmutamiseks on kasutatud resonantselt ergastatud Ramani joonte intensiivsust ja neeldumise intensiivsust. Aegsõltuvust on uuritud erineval temperatuuril ja ergastusvõimsusel. On käsitletud füüsikalist mudelit, mis on seotud molekulaariooni ionisatsiooniga ja mis selgitab kvalitatiivselt eksperimentaalandmeid.

ФОТОИНДУЦИРОВАННАЯ НЕСТАБИЛЬНОСТЬ МОЛЕКУЛЯРНЫХ ДЕФЕКТОВ MnO₄⁻ В ЙОДИСТОМ КАЛИИ

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Рассмотрена нестабильность молекулярного иона MnO₄⁻ в кристалле KI под интенсивным резонансным возбуждением в оптическом переходе ${}^1A_1 \rightarrow {}^1T_2$ дефекта. Для проявления временной зависимости этого эффекта использовались интенсивности резонансно возбужденных рамановских линий и интенсивность поглощения. Временная зависимость была исследована при разных температурах и мощностях возбуждения. Обсуждалась связанная с ионизацией молекулярного иона физическая модель, которая качественно объясняет экспериментальные данные.