Raman scattering by hydride and deuteride ion local modes in calcium and strontium fluoride

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Abstract. A simple enhancement technique which was found to increase Raman scattered signals from local modes of hydride and deuteride ions in CaF_2 and SrF_2 by a factor of up to five is described. It enabled the fundamental and all three second harmonic transitions of both hydride and deuteride ions located in the tetrahedral $\overline{T}_d$ sites to be observed. Anharmonic potential well constants for these sites are reported.

1. Introduction

It is well established that hydrogen and deuterium in the form of negative ions substitute for fluoride ions in the regular lattice site of tetrahedral $\overline{T}_d$ symmetry. Infrared spectra have been observed by Elliott et al [1], who found for CaF_2 a fundamental, one second harmonic and two third harmonic transitions, which is consistent with the electric dipole selection rules for an anharmonic oscillator with $\overline{T}_d$ symmetry. From this data they determined the four potential well constants, A, B, C_1 and C_2, for an H^- ion vibrating in a tetrahedral symmetry site. The energies of other transitions were then predicted using these constants.

Transitions to the other two second harmonic levels have been directly observed by Hayes and Macdonald [2] by applying a uniaxial stress to the sample. The locations of all three second harmonic energy levels have been subsequently confirmed by Lee and Faust [3] using two CO_2 lasers in a two photon step process. One laser was used to saturate the fundamental energy level and the other laser to observe stepwise absorption from this level to the second harmonic levels.

In principle, Raman scattering can be used to measure the energies of the fundamental, all three second harmonic and all four third harmonic transitions, which are all Raman active. Using this technique, Harrington et al [4] observed the fundamental and two of the three second harmonic transitions for hydride ions in both CaF_2 and SrF_2. For deuteride ions in CaF_2 and SrF_2, they observed only the fundamental and the fundamental and one second harmonic respectively.

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In this paper, the Raman spectra of hydrogenated and deuterated crystals of calcium and strontium fluoride are reported in Section 3 for the same substitutional tetrahedral site H^- and D^- local modes. These spectra were obtained using an enhancement technique, described in Section 2, to increase the Raman signal.

The data obtained allows the calculation of the anharmonic potential well constants, up to quartic, from the energies of the fundamental and second harmonic levels only. These results are tabulated in Section 4.

2. Experimental

The calcium and strontium fluoride crystals used in this investigation also contained 0.05% or 0.1% of the rare earth gadolinium, which was required for other studies, and were grown at the University of Canterbury using the Stockbarger method. Hydrogen or deuterium was diffused into the crystals by the method of Hall and Schumacher [5].

The Raman measurements were obtained using an 18 watt Spectra Physics laser with an Anaspec 300S laser filter monochromator to remove the laser plasma lines. Most spectra were obtained with 2 to 3 watts of the 488.0 nm laser line. The Raman scattered light was collected in a 90° scattering geometry with f/6.5 optics. The collected light was analysed using a double Spex 1403 spectrometer fitted with a thermoelectrically cooled RCA C31034A photomultiplier tube and a PAR Model 1112 photon counting system. All samples were cooled to 14 K using a Cryodyne Model 22 closed cycle helium refrigerator cryostat.

In order to enhance the Raman signal of the hydrogenated or deuterated samples, three crystal faces were first polished and then either aluminised or silvered by metal vapour deposition. The laser beam enters the crystal through a small opening in the metal vapour deposited layer at the end of one of the two parallel faces and undergoes multi-reflections (figure 1). The Raman scattered light from each of these successively reflected laser beams is augmented by reflection from the back surface. This increased the Raman signal by a factor of up to five over the usual single laser beam arrangement.
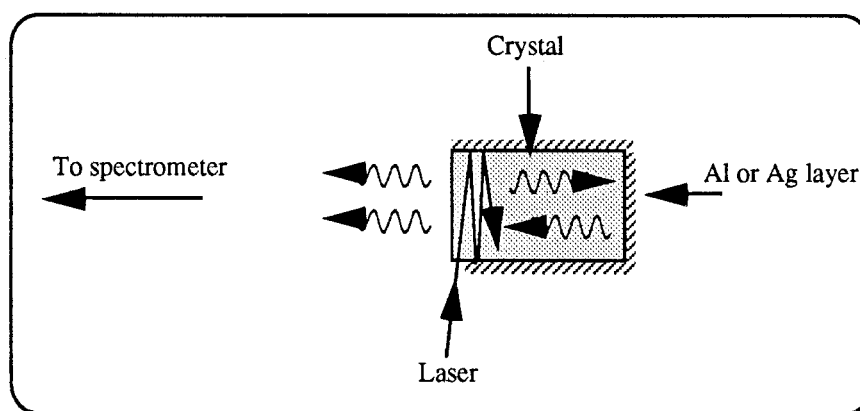

Figure 1. Experimental configuration of laser and sample to enhance the Raman signal.

Under ideal conditions the expected increase could be as much as forty times. Loss of laser light in each successive reflection from the non-ideal surfaces limits the gain obtained.

3. Raman measurements

The Raman scattering spectra by the H^- and D^- local modes were obtained using either the multi-reflection technique described above, or by reflection from the back surface of the crystal only, to enhance the signal. This, along with integration times of up to 100 seconds, gave sufficient sensitivity to enable the fundamental and all three second harmonic transitions to be observed for both hydride and deuteride ions in both CaF_2 and SrF_2 crystals. The three second harmonic local mode lines can be clearly seen in the spectra shown in figure 2. Where appropriate, background fluorescence has been removed from the spectra to unambiguously show the Raman features.
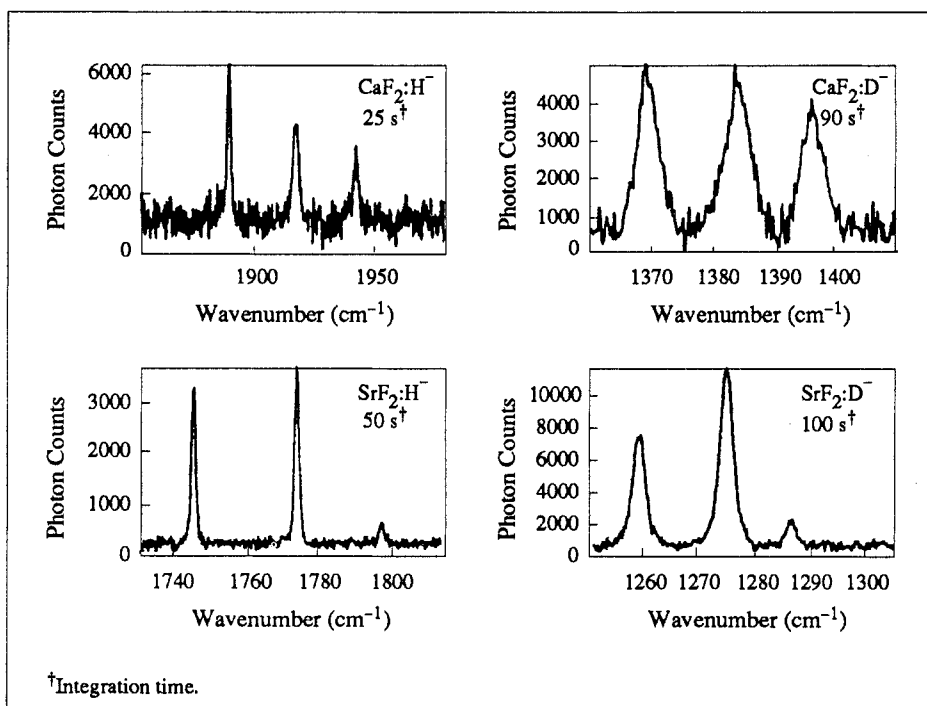

Figure 2. Raman scattered second harmonic $\overline{T}_d$ local mode lines in CaF_2 and SrF_2 at 14K.

The peak positions (table 1) agree with those obtained from infrared absorption by Elliott *et al* [1] and Hayes and Macdonald [2] and also with the Raman measurements of Harrington *et al* [4]. The relative intensities and linewidths (table 1) were obtained by curve fitting the Raman lines to Lorentzian lineshapes. The Raman signal to noise ratio is a factor of three better for the second harmonic local mode lines in SrF_2 than in CaF_2.

Table 1. Peak positions (cm^{-1}) and linewidths (cm^{-1}) at 14 K of the $\overline{T}_d$ site Raman lines of H$^-$ and D$^-$ ions in CaF$_2$ and SrF$_2$.

crystal	line	symmetry	peak position	width	rel. intensity
CaF$_2$:H$^-$	fundamental	Γ_5	965.2 ± .3	3.45 ± .10	18 ± 4
		Γ_1	1891.5 ± .5	1.59 ± .08	1.75 ± .47
	2nd harmonic	Γ_5	1919.0 ± .7	2.34 ± .15	1.72 ± .50
		Γ_3	1943.6 ± .6	2.17 ± .22	1.00 ± .36
CaF$_2$:D$^-$	fundamental	Γ_5	694.6 ± .3	3.28 ± .10	15 ± 2
		Γ_1	1369.2 ± .4	3.06 ± .18	1.32 ± .30
	2nd harmonic	Γ_5	1383.7 ± .5	3.58 ± .21	1.42 ± .32
		Γ_3	1395.6 ± .6	3.09 ± .24	1.00 ± .26
SrF$_2$:H$^-$	fundamental	Γ_5	892.8 ± .3	1.41 ± .20[†]	64 ± 23
		Γ_1	1745.0 ± .4	1.19 ± .03[†]	6.6 ± 2.5
	2nd harmonic	Γ_5	1774.6 ± .4	1.30 ± .03[†]	8.0 ± 3.0
		Γ_3	1799.5 ± .6	1.34 ± .26[†]	1.00 ± .67
SrF$_2$:D$^-$	fundamental	Γ_5	639.9 ± .3	2.16 ± .10	116 ± 47
		Γ_1	1259.1 ± .4	2.25 ± .08	8.2 ± 3.6
	2nd harmonic	Γ_5	1275.3 ± .4	2.33 ± .05	13.5 ± 5.6
		Γ_3	1287.2 ± .6	1.24 ± .28[†]	1.00 ± .76

[†]Instrument limited

The relative intensities of the three second harmonics for the hydride ions are about the same as those for the deuteride ions in both calcium and strontium fluoride crystals. However, the intensities of the two lower energy second harmonic transitions relative to the highest energy second harmonic transition are stronger in SrF$_2$ than in CaF$_2$.

The linewidths of the Raman scattered local mode lines are greater for D$^-$ than for H$^-$ consistent with broadening by anharmonic decay of the D$^-$ and H$^-$ local mode excitations into two and three lattice modes respectively [1]. The broader linewidths obtained here compared with Elliott *et al's* [1] infrared measurements are attributed to the collective effects of spectrometer linewidth, laser linewidth and concentration broadening of the local mode transitions. Harrington *et al* [4] show at low concentrations of H$^-$ that the Raman and infrared lines do have the same width.

A search made for third harmonic local mode lines failed to reveal any of these very weak transitions.

The two tetragonal $\overline{C}_{4v}$ symmetry site fundamental local mode lines, corresponding to the H$^-$ or D$^-$ ions in the nearest neighbour interstitial charge compensation site adjacent to the trivalent gadolinium, were also observed for CaF$_2$. These are given in table 2 and are in substantial agreement with those obtained by Raman scattering by Van Dyk [6] and with the infrared measurements of Jones *et al* [7].

Table 2. Peak positions (cm^{-1}) and linewidths (cm^{-1}) at 14 K of the $\overline{C}_{4v}$ site fundamental Raman lines of H$^-$ and D$^-$ ions in CaF$_2$.

crystal	symmetry	peak position	width	rel. intensity
CaF$_2$:Gd(0.05%):H$^-$	γ_5	1018.3 ± 0.3	1.2 ± 0.1†	2.0 ± 0.3
	γ_1	1105.4 ± 0.5	3.8 ± 0.2	1.0 ± 0.2
CaF$_2$:Gd(0.05%):D$^-$	γ_5	737.9 ± 0.3	3.5 ± 0.2	1.0 ± 0.2
	γ_1	801.5 ± 0.3	3.7 ± 0.2	1.0 ± 0.2

†Instrument limited

4. Anharmonic potential well analysis for the $\overline{T}_d$ site

The potential for a single particle vibrating in a potential well of $\overline{T}_d$ symmetry, up to the quartic terms, has been given by Elliott *et al* [1] as

$$V = A(x^2 + y^2 + z^2) + B(xyz) + C_1(x^4 + y^4 + z^4) + C_2(y^2z^2 + z^2x^2 + x^2y^2),$$

where x, y, z are the light ion displacements. Energies of the associated Hamiltonian to second order in the cubic terms and first order in the quartic terms have been given by these authors. Their experimental infrared data for H$^-$ in CaF$_2$ was sufficient to determine the four potential well constants A, B, C_1 and C_2.

With the Raman local mode data given in table 1, a least squares analysis was carried out to determine the potential well constants from the energies of the fundamental and three second harmonic transitions only. The cases of H$^-$ and D$^-$ were first fitted separately and similar parameters are obtained from the two respective exact fits justifying the single particle static well approximation used by Elliott *et al* [1]. These parameters accurately predict the energies of the third harmonic transitions observed in the infrared [1], with the exception of the CaF$_2$:H$^-$ Γ_5 level, where there is a 3 cm^{-1} difference. Fitting both the H$^-$ and D$^-$ Raman data simultaneously yields the potential well parameters for CaF$_2$ and SrF$_2$ given in table 3. In this combined H$^-$ and D$^-$ ion analysis, the harmonic frequencies, ω_H and ω_D, of the H$^-$ and D$^-$ ion oscillators respectively, are treated as adjustable parameters. Excellent agreement is obtained between the calculated and all measured energy levels. In general, it was found that the cubic parameter B gave anharmonic shifts up to four times greater than the quartic C_1 parameter which in turn gave shifts up to five times those given by the quartic C_2 parameter. Hence, the energy levels of the $\overline{T}_d$ local modes in CaF$_2$ and SrF$_2$ are not very sensitive to the parameter C_2. By an identical analysis using Elliott *et al's* [1] data for CaF$_2$, the parameters in table 4 were obtained.

While the potential well parameters obtained for the CaF$_2$ Raman data are very similar to those of Elliott *et al* [1], discrepancies are apparent with those reported by Hayes and Macdonald [2] for SrF$_2$. Their parameters give energy levels close to the infrared data of Elliott *et al*; however, there are differences of up to 8 cm^{-1} with the second harmonic energy levels obtained from the Raman data reported here. As the data used to calculate these parameters was not given by Hayes and Macdonald [2] it is not possible to resolve

Table 3. The tetrahedral oscillator potential well constants and the vibrational energy levels of H^- and D^- ions in CaF_2 and SrF_2 at 14 K calculated using the Raman data in table 1. Note the uncertainties given for the potential well constants are the most probable error.

CaF_2

$\omega_D = 702.0 \pm 0.4 \text{ cm}^{-1}$ $C_1 = (-2.55 \pm 0.22) \times 10^{20} \text{ J m}^{-4}$
$\omega_H = 981.3 \pm 0.8 \text{ cm}^{-1}$ $C_2 = (0.8 \pm 1.2) \times 10^{20} \text{ J m}^{-4}$
     $|B| = (8.35 \pm 0.08) \times 10^{11} \text{ J m}^{-3}$

n	Symmetry	Observed H^- Energies (cm^{-1})	Calculated H^- Energies (cm^{-1})	Observed D^- Energies (cm^{-1})	Calculated D^- Energies (cm^{-1})
1	Γ_5	965.2 ± 0.3	965.4	694.6 ± 0.3	694.4
2	Γ_1	1891.5 ± 0.5	1891.0	1369.2 ± 0.4	1369.8
2	Γ_5	1919.0 ± 0.7	1919.3	1383.7 ± 0.5	1383.3
2	Γ_3	1943.6 ± 0.6	1943.8	1395.6 ± 0.6	1395.0
3	Γ_5	$(2825.6 \pm 0.8)^\dagger$	2821.0	$(2047. \pm 1)^\dagger$	2047.3
3	Γ_1		2861.7		2066.8
3	Γ_4		2886.3		2078.5
3	Γ_5	$(2912.2 \pm 0.5)^\dagger$	2912.8	$(2093. \pm 1)^\dagger$	2091.1

†Data of Elliot et al [1] at 20K, included for comparison.

SrF_2

$\omega_D = 647.3 \pm 0.5 \text{ cm}^{-1}$ $C_1 = (-2.12 \pm 0.24) \times 10^{20} \text{ J m}^{-4}$
$\omega_H = 908.0 \pm 1.0 \text{ cm}^{-1}$ $C_2 = (3.2 \pm 1.1) \times 10^{20} \text{ J m}^{-4}$
     $|B| = (7.48 \pm 0.07) \times 10^{11} \text{ J m}^{-3}$

n	Symmetry	Observed H^- Energies (cm^{-1})	Calculated H^- Energies (cm^{-1})	Observed D^- Energies (cm^{-1})	Calculated D^- Energies (cm^{-1})
1	Γ_5	892.8 ± 0.3	892.8	639.9 ± 0.3	639.9
2	Γ_1	1745.0 ± 0.4	1744.6	1259.1 ± 0.4	1259.9
2	Γ_5	1774.6 ± 0.4	1774.9	1275.3 ± 0.4	1274.6
2	Γ_3	1799.5 ± 0.6	1799.7	1287.2 ± 0.6	1286.6
3	Γ_5		2602.2		1882.8
3	Γ_1		2646.1		1904.2
3	Γ_4		2671.0		1916.1
3	Γ_5		2697.6		1928.9

these differences.

The anharmonic shifts in the energy levels are reduced by about 7% in SrF_2 compared to CaF_2. The ratio of the harmonic frequencies, ω_H/ω_D, in SrF_2 (1.403 ± 0.003) is greater than that for CaF_2 (1.398 ± 0.002) which indicates that the D^- local modes are not as extended in SrF_2 as in CaF_2. This can be qualitatively explained by the greater mass of the Sr^{2+} ion compared to the Ca^{2+} ion in the respective crystal lattices.

Table 4. The tetrahedral oscillator potential well constants for H^- and D^- ions in CaF_2 obtained using the 20K infrared data of Elliot *et al* [1].

$\omega_D = 702.1 \pm 0.7$ cm^{-1}	$C_1 = (-2.43 \pm .17) \times 10^{20}$ J m^{-4}
$\omega_H = 981.0 \pm 1.3$ cm^{-1}	$C_2 = (-0.1 \pm 2.2) \times 10^{20}$ J m^{-4}
	$|B| = (8.09 \pm 0.17) \times 10^{11}$ J m^{-3}

The Raman local mode lines in BaF_2:H^- and D^- were not measured because no suitable samples were available. However, since Newman [8] questions the parameters obtained by Harrington *et al* [4], a least squares analysis was carried out using Harrington's data. When fitting the H^- and D^- data simultaneously, difficulty was experienced in getting the least squares analysis to converge and the quartic anharmonic parameters obtained were an order of magnitude larger than those obtained for the other alkaline earth fluorides. It appears essential that all three second harmonic levels are required to obtain reliable parameters. As the parameters given by Harrington *et al* [4] were found to give calculated levels up to 45 cm^{-1} from those measured by them, there appears to be an error. The parameters of Hayes and Macdonald [2] give the observed energy levels to within 7 cm^{-1}.

5. Conclusion

Raman spectroscopy of local modes is a useful technique that complements and supplements infrared absorption measurements. For the case of the H^- and D^- ions in sites of $\overline{T}_d$ symmetry in the alkaline earth fluorides, both the fundamental and all three second harmonics can be measured. This allows reliable potential well parameters to be calculated independently of the energies of any of the weak infrared transitions to the third harmonic energy levels.

Acknowledgements

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