Inorganica Chimica Acta, *99* (1985) 37–42

Indirect Assignment of the Infrared Spectrum of K_2ReF_6

MARCO BETTINELLI, LORENZO DI SIPIO*, ANTONIO PASQUETTO
Istituto di Chimica Generale ed Inorganica, Facoltà di Scienze MM. FF. e NN., Università di Padova, Padua, Italy
GIANLUIGI INGLETTO
Istituto di Biochimica, Facoltà di Medicina Veterinaria, Università di Parma, Parma, Italy
and ANGELO MONTENERO
Istituto di Strutturistica Chimica, Facoltà di Scienze MM. FF. e NN., Università di Parma, Parma, Italy

Received July 20, 1984

Abstract

The infrared (IR) spectrum of K_2ReF_6 was recorded at room temperature and 10 K. The spectral data confirm the presence of a trigonal distortion acting on the ReF_6^{2-} anion. By means of the analysis of the hot bands present in the polarized electronic absorption spectra measured at different temperatures, it was possible to unequivocally assign the symmetries of the internal and lattice modes active in the IR spectrum.

Introduction

The vibrational spectra of hexahalide complexes of transition metal ions have been widely studied [1]. In the case of octahedral (O_h) surroundings, all the vibrational symmetries are definitely assigned, whereas when the site symmetries around the central ion are lower, the splitting pattern of the vibrations which are degenerate in O_h symmetry may still be uncertain.

Concerning the Raman active vibrations, the linearly polarized light allows the correct assignment of the components of the split bands [2]. On the other hand, this is not generally possible in the case of IR spectra. It is our opinion that this situation can be overcome by the analysis of the hot bands which may be present in the electronic absorption spectra of these complexes. By means of this analysis it is possible to determine also the symmetries of the IR active lattice vibrations.

In order to confirm this opinion, we examined pure K_2ReF_6 single crystals and measured the IR and the polarized electronic absorption spectra at different temperatures in the short range 16950–18020 cm^{-1} in which we identified and assigned the hot band structure. This result allowed us to assign unambiguously the IR spectrum, as well as the optical lattice vibrations.

The choice of this compound was due to the following considerations: K_2ReF_6 crystals belong to the *P$\bar{3}$m1* space group with one molecule in the unit cell and a local site distortion is present, due to a static D_{3d} symmetry perturbation superimposed on the O_h crystalline field around the Re^{4+} ion [3]. The pure crystals are uniaxial thus enabling the measurement of the linearly polarized electronic absorption spectra.

Experimental

Good K_2ReF_6 single crystals were prepared following Peacock [4]. The crystals were grown during a twenty day period from an aqueous solution at 40 °C. The room temperature IR spectrum was measured using, in the low energy region (50–450 cm^{-1}), an IR Bruker spectrophotometer mod. IFS 113 V, and a Perkin-Elmer spectrophotometer mod. 580 B for the high energy region (450–800 cm^{-1}). The low temperature (10 K) IR spectrum in the range 200–800 cm^{-1} was measured using a Jasco DS-702 G spectrophotometer equipped with a CTI-Cryogenics mod. 21 refrigerator (Helix Company). The samples were included in a Nujol mull on polyethylene and CsI, to measure the low and high energy spectra respectively.

The electronic absorption spectra at different temperatures were measured using a Cary 17 spectrophotometer equipped with an Oxford Instruments CF 204 continuous flow Helium cryostat. The incidental light was polarized by a calcite Glan Thomson polarizer and the spectra were recorded with the electric ($\vec{E}$) and magnetic ($\vec{H}$) vectors either parallel or perpendicular to the *c* crystallographic axis. The orientation of the crystal axes was previously checked by taking Weissenberg photographs.

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*Author to whom correspondence should be addressed.

0020-1693/85/$3.30

The single crystals used in the measurements of the α spectra ($\vec{E}\perp c$; $\vec{H}\perp c$ were less thick than those used for the $\sigma(\vec{E}\perp c; \vec{H} /\!/ c)$ and $\pi(\vec{E} /\!/ c; \vec{H}\perp c)$ spectra.

Results

Description of the Spectra

The low (50–450 cm^{-1}) and the high (450–800 cm^{-1}) energy regions of the room temperature IR spectrum are reported in Figs. 1 and 2 respectively. The 10 K IR spectrum in the 200–800 cm^{-1} range is not reported because it is quite similar to the one measured at room temperature.

The spectrum shows twelve peaks and two shoulders. Their wavenumbers and the proposed assignments are reported in Table I.

The electronic polarized spectra at 4.2 K, 120 K and room temperature in the range 590–555 nm (16950–18020 cm^{-1}) are reported in Figs. 3–5.

From their analysis, it is clear that the bands, whose energy is lower than the energy of the peak at 17621 cm^{-1}, are hot bands as they disappear at 4.2 K. The wavenumbers of the analyzed peaks and the assignments of the hot band structure are given in Table II.

Discussion

IR Spectrum

The irreducible representations for $\vec{k} = 0$ vibrational modes of K_2ReF_6, on the basis of the factor group analysis, are reported in Table III.

The a_{2u} and e_u symmetry modes are infrared active and in the IR spectrum seven bands are expected. The irreducible representations for the 15 internal modes of an octahedral ReF_6^{2-} ion are:

$\Gamma(ReF_6^{2-}, O_h \text{ symmetry}) = a_{1g} + e_g + t_{2g} + 2t_{1u} + t_{2u}$ and only the two t_{1u} modes are infrared active. However, as the actual symmetry of the ReF_6^{2-} moiety in crystalline K_2ReF_6 is D_{3d}, the two active t_{1u} modes and the inactive one t_{2u} split into the a_{2u}, e_u and the a_{1u}, e_u components respectively.

The IR spectrum of K_2ReF_6 does not show any substantial changes with temperature. This means that the compound does not undergo any structural phase transition down to 10 K.

The spectrum is quite similar to those measured for related compounds [5] with respect to their internal modes and so we can follow the commonly accepted interpretative scheme in order to make a preliminary assignment.

The intense doublet (222 and 257 cm^{-1}) is assigned to the a_{2u} and e_u split components of the $\nu_4(t_{1u})$ octahedral bending mode and likewise the very strong peak (543 cm^{-1}) and its shoulder (565 cm^{-1}) are assigned to the a_{2u} and e_u components of the $\nu_3(t_{1u})$ octahedral stretching mode.

The medium intense peaks at 722 cm^{-1} and 738 cm^{-1} are interpreted as combination bands between the Raman active $\nu_2(e_g)$ internal mode (539 cm^{-1}) present in the Raman spectra of K_2ReF_6 [6] and in the spectra of related compounds [7] and the components e_u and a_{1u} (IR inactive) corresponding to the IR inactive $\nu_6(t_{2u})$ octahedral bending mode. The calculated wavenumbers for the split components are 183 and 199 cm^{-1} respectively.

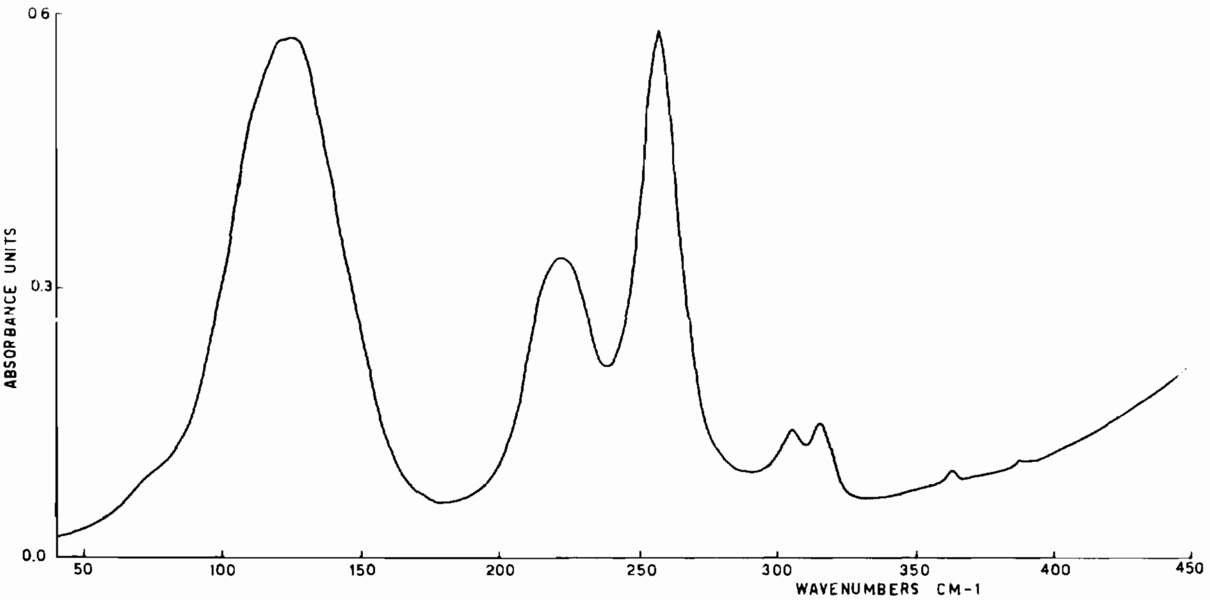

Fig. 1. Low energy region of the room temperature IR spectrum of K_2ReF_6.

The low energy region of the spectra shows a broad and strong band centered at 123 cm^{-1} with a small shoulder at 63 cm^{-1}. These bands cannot be ascribed to internal modes, owing to their low energy and can be assigned as the optical branch translatory lattice modes a_{2u} and e_u. The assignments of the other weak bands are proposed as intercombinations between gerade and ungerade modes on the basis of the results of the Raman spectrum [6].

From the analysis of the spectrum it is evident that the trigonal distortion splits the internal modes that are triply degenerate in O_h symmetry, but it is not sufficient to activate the e_u component arising from the IR inactive $\nu_6(t_{2u})$ octahedral mode.

Hot Bands

The electronic absorption spectra measured at 4.2 K show a band at 17621 cm^{-1} assigned as

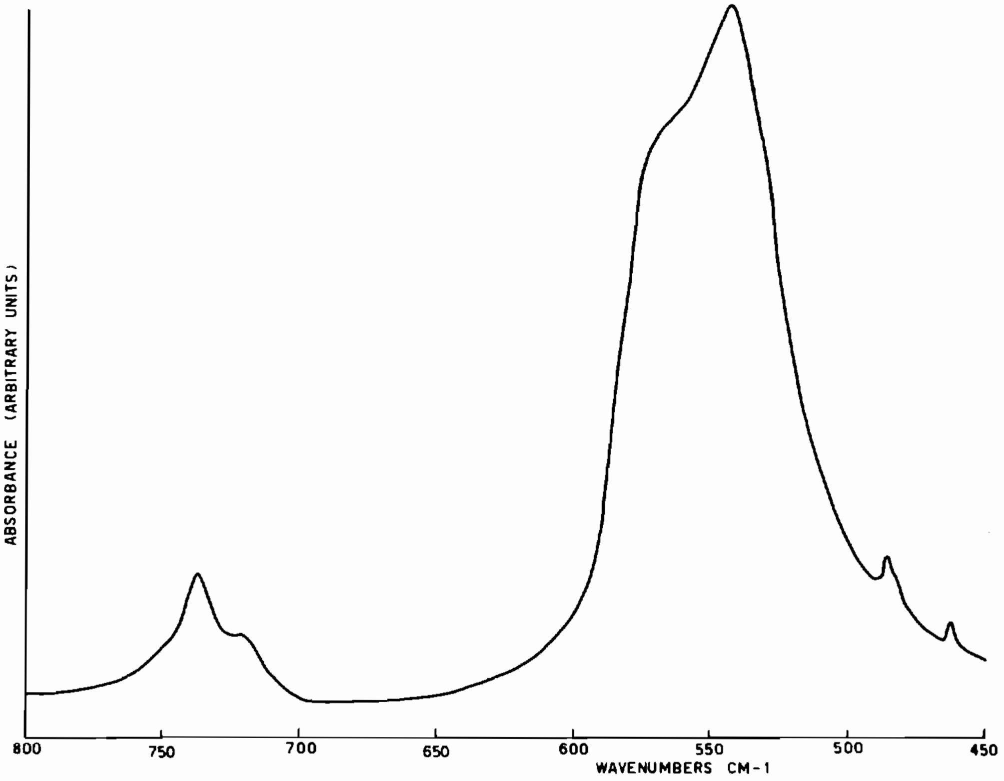

Fig. 2. High energy region of the room temperature IR spectrum of K_2ReF_6.

TABLE I. Infrared Spectrum of K_2ReF_6.

Observed frequencies (cm^{-1})	Calculated frequencies (cm^{-1})	Assignment
63(sh)vw		a_{2u}(lattice)
123s		e_u(lattice)
222s		$a_{2u}(\nu_4)$
257s		$e_u(\nu_4)$
305w	305	a_{2u}(lattice) + $e_g(\nu_5)$
314w	318	$a_{1u}(\nu_6)$ + e_g or a_{1g}(lattice, 119 cm^{-1})
363vw	365	e_u(lattice) + $e_g(\nu_5)$
388vw	395	$a_{1u}(\nu_6)$ +
388vw	395	$a_{1u}(\nu_6)$ + e_g or a_{1g}(lattice, 119 cm^{-1}) + e_g or a_{1g}(lattice, 77 cm^{-1})
463w	464	$a_{2u}(\nu_4)$ + $e_g(\nu_5)$
486w	499	$e_u(\nu_4)$ + $e_g(\nu_5)$
543vs		$e_u(\nu_3)$
565(sh)vs		$a_{2u}(\nu_3)$
722m		$e_g(\nu_2)$ + $e_u(\nu_6)$
738m		$e_g(\nu_2)$ + $a_{1u}(\nu_6)$

the O–O line of the transition from the ground state $(\Gamma_5^+ + \Gamma_6^+)[\Gamma_8^+(^4A_{2g})]$ to the $\Gamma_4^+[\Gamma_7^+(^2T_{2g})]$ excited state [8]. In the spectra measured at 120 K there is a set of peaks in the lower energy side with respect to the O–O line, which disappears at 4.2 K. The majority of these peaks are due to vibronic transitions from ungerade vibrational states thermally populated lying over the electronic ground state, as shown in Table II. On the basis of the selection rules, the symmetries of the activating vibrations are unequivocally determined as a_{2u}(lattice), e_u(lattice), $a_{1u}(\nu_6)$ and $e_u(\nu_4)$ modes.

On the other hand, the peak present at 17454 cm^{-1} ($\Delta\tilde{\nu}$ = −167, T = 120 K) is assigned as the O–O line of the transition from the thermally populated $\Gamma_4^+[\Gamma_8^+(^4A_{2g})]$ electronic state to the $\Gamma_4^+[\Gamma_7^+(^2T_{2g})]$ excited state. This interpretation is confirmed by the presence of the hot band at 17987 cm^{-1} assigned to the vibronic transition from the $\Gamma_4^+[\Gamma_8^+(^4A_{2g})]$ state to the vibrational state lying 533 cm^{-1} over the aforementioned electronic excited state. The symmetry of this vibration is determined from the analysis of the band at 17086 cm^{-1} ($\Delta\tilde{\nu}$ = −535) present in the room temperature electronic spectra. It is due to the transition from the vibrational state that lies 535 cm^{-1} over the electronic ground state to the $\Gamma_4^+[\Gamma_7^+(^2T_{2g})]$ excited state. From the selection

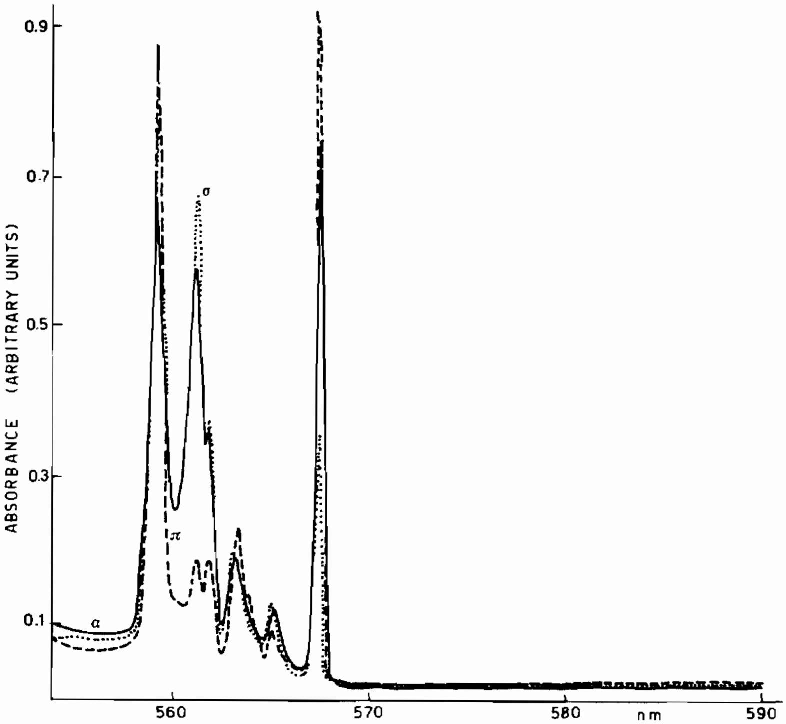

Fig. 3. Linearly polarized absorption spectra at 4.2 K of a pure K_2ReF_6 crystal in the range 590–555 nm.

TABLE II. Transition Energies and Assignments of the Hot Band Structure in the Linearly Polarized Spectra of a Pure K_2ReF_6 Crystal at Various Temperatures.

No.	λ/nm	$\tilde{\nu}$/cm^{-1}	$\Delta\tilde{\nu}$	T/K	Polarization	Assignment	Symmetry of the activating vibration
1	585.3	17086	−535	R.T.	α, σ, π	$(\Gamma_5^+ + \Gamma_6^+)[\Gamma_8^+(^4A_{2g})] \rightarrow \Gamma_4^+[\Gamma_7^+(^2T_{2g})]$	$e_u(\nu_3)$
2	575.8	17366	−255	120,R.T.	α, σ, π	$(\Gamma_5^+ + \Gamma_6^+)[\Gamma_8^+(^4A_{2g})] \rightarrow \Gamma_4^+[\Gamma_7^+(^2T_{2g})]$	$e_u(\nu_4)$
3	573.9	17425	−196	120,R.T.	α, σ	$(\Gamma_5^+ + \Gamma_6^+)[\Gamma_8^+(^4A_{2g})] \rightarrow \Gamma_4^+[\Gamma_7^+(^2T_{2g})]$	$a_{1u}(\nu_6)$
4	572.9	17454	−167	120,R.T.	α, σ, π	$\Gamma_4^+[\Gamma_8^+(^4A_{2g})] \rightarrow \Gamma_4^+[\Gamma_7^+(^2T_{2g})]$(O–O)	–
5	571.6	17495	−126	120,R.T.	α, σ, π	$(\Gamma_5^+ + \Gamma_6^+)[\Gamma_8^+(^4A_{2g})] \rightarrow \Gamma_4^+[\Gamma_7^+(^2T_{2g})]$	e_u(lattice)
6	569.5	17558	−63	120,R.T.	α, σ	$(\Gamma_5^+ + \Gamma_6^+)[\Gamma_8^+(^4A_{2g})] \rightarrow \Gamma_4^+[\Gamma_7^+(^2T_{2g})]$	a_{2u}(lattice)
7	567.5	17621	0	4.2,120,R.T.	α, σ, π	$(\Gamma_5^+ + \Gamma_6^+)[\Gamma_8^+(^4A_{2g})] \rightarrow \Gamma_4^+[\Gamma_7^+(^2T_{2g})]$ (O–O)	–
8	556.0	17987	533[a]	120,R.T.	α, σ, π	$\Gamma_4^+[\Gamma_8^+(^4A_{2g})] \rightarrow \Gamma_4^+[\Gamma_7^+(^2T_{2g})]$	$e_u(\nu_3)$

[a] $\Delta\tilde{\nu}$ from peak 4.

rules, the symmetry of the vibration is determined as e_u.

The symmetry assignment of the ungerade vibrations which are responsible of the vibronic hot bands permits the definition of the symmetries of the other IR active vibrations. The IR active band at 222 cm^{-1} was identified as a split component of the $\nu_4(t_{1u})$ octahedral vibration. As the other component was previously assigned as a e_u mode, the symmetry of the considered vibration is a_{2u}.

Similarly, the shoulder present at 565 cm^{-1} in the IR spectrum and arising from the splitting of the $\nu_3(t_{1u})$ octahedral vibration is assigned as a a_{1u} mode, as the other component was previously assigned as a e_u mode from the analysis of the electronic hot bands.

The vibrational mode (calculated wavenumber = 183 cm^{-1}) which was assigned as a split component of the inactive $\nu_6(t_{2u})$ mode, turns out to be a e_u mode as the other component was identified as a a_{1u} symmetry vibration.

The symmetries of the internal and lattice ungerade modes are summarized in Table I.

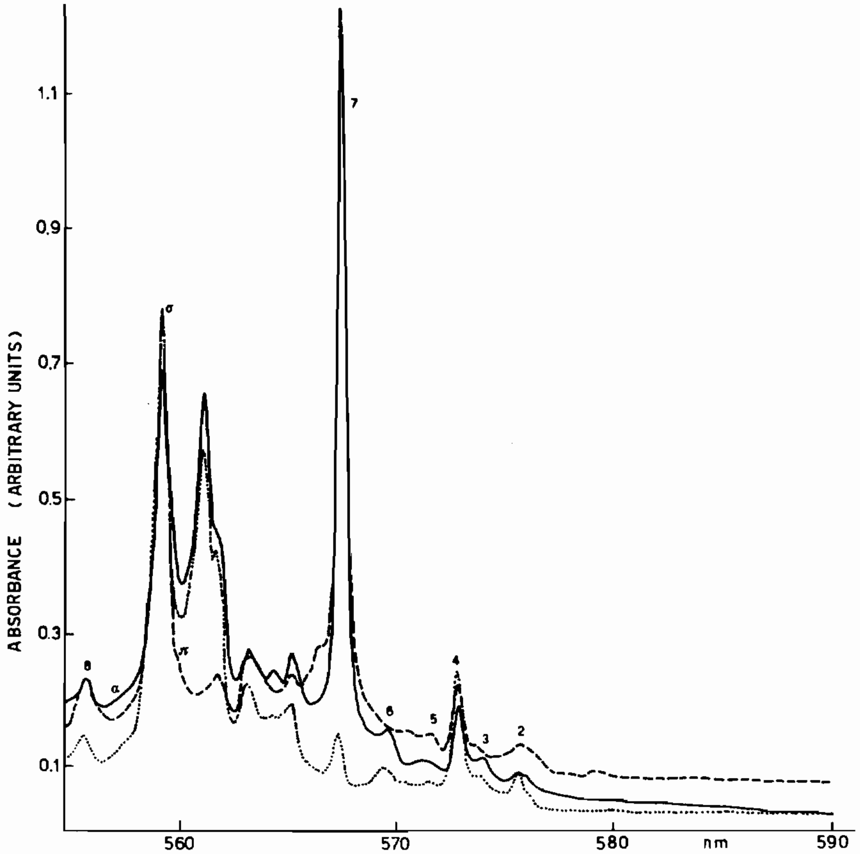

Fig. 4. Linearly polarized absorption spectra at 120 K of a pure K_2ReF_6 crystal in the range 590–555 nm.

TABLE III. Classification of the Vibrational Modes of K_2ReF_6.

Types of mode	Symmetries in D_{3d}
Internal $ReF_6{}^{2-}$	$a_{1g}(\nu_1) + a_{1g}(\nu_5) + e_g(\nu_2) + a_{1u}(\nu_6) + a_{2u}(\nu_3) + a_{2u}(\nu_4) + e_u(\nu_3) + e_u(\nu_4) + e_u(\nu_6)$
Vibrational lattice	$a_{1g} + e_g + e_u + a_{2u}$
Rotational lattice	$e_g + a_{2g}$
Acoustic	$a_{2u} + e_u$

For the internal modes, we report in brackets the corresponding labels in O_h symmetry.

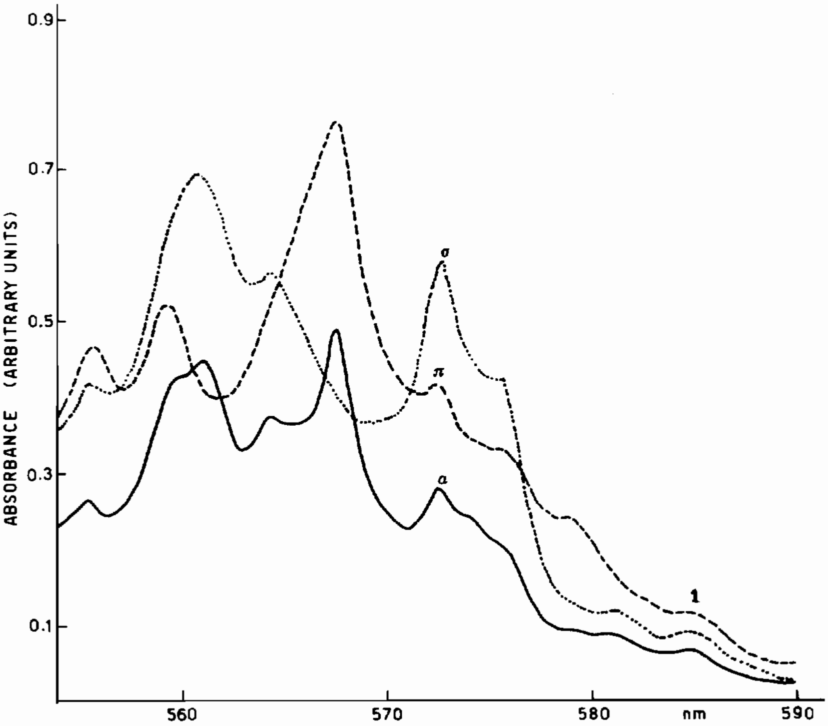

Fig. 5. Linearly polarized absorption spectra at room temperature of a pure K_2ReF_6 crystal in the range 590–555 nm.

Conclusions

We were able, by means of a careful analysis of the hot bands present in the electronic polarized absorption spectra of K_2ReF_6 crystals measured at 120 K and room temperature to define unamambiguously the symmetry of the vibrations which activate the vibronic transitions. This attribution allows us to assign indirectly the symmetry of the vibrational modes present in the IR spectrum.

Acknowledgments

This work was carried out with the financial support of M.P.I. (Italian Ministry of Education) and of C.N.R. (Italian National Research Council).

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