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N. Edelstein

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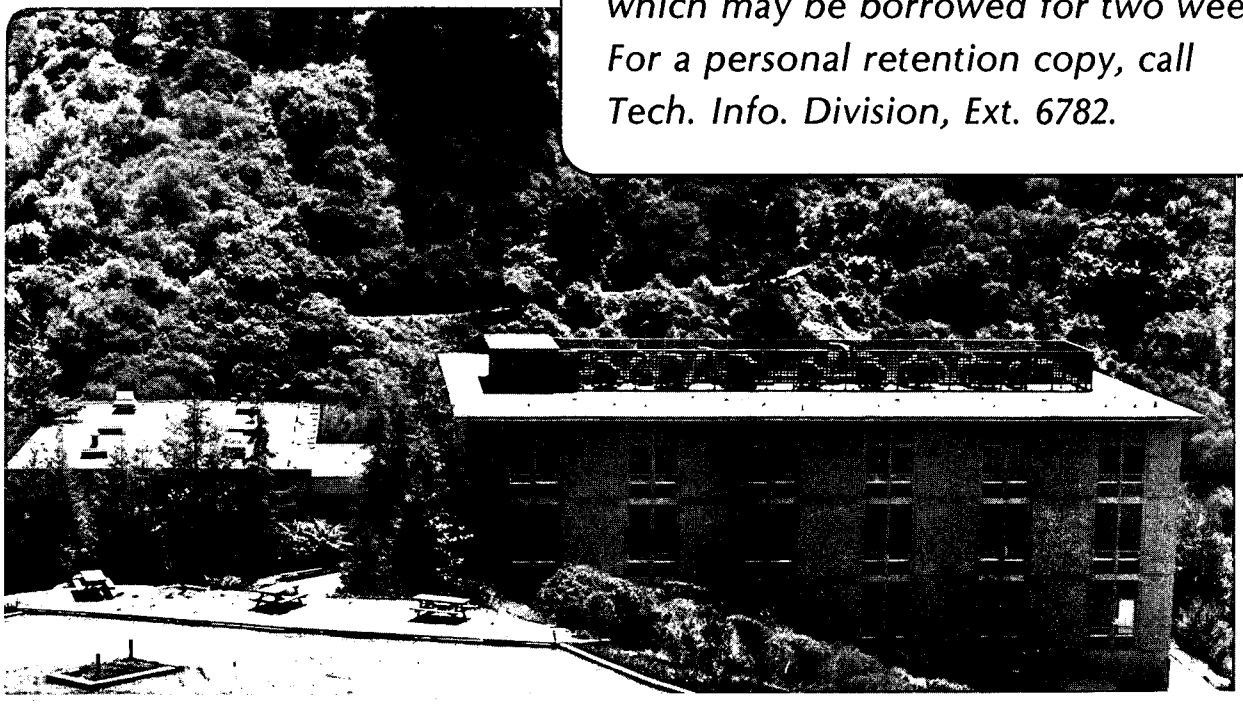

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LBL-16326

Site Selective Excitation of U^{4+} Diluted in Incommensurate $ThBr_4$

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Abstract

Selective excitation experiments in the visible region are reported for the U^{4+}:$ThBr_4$ system. These permit the classification of absorption and emission lines to the sites found in the incommensurately modulated structure of $ThBr_4$. The lines are assigned to a D_{2d} (B) site, a continuous distribution of D_2 (C) sites, and to the limiting D_2 (A) site. By application of the model of Delamoye and Currat (J. Physique-Lettres 43, L655 (1982)), the energy levels have been mapped as a function of the phase angle, ϕ_ℓ, of the distortion. The agreement between the predictions of the model and experiment is very good. It is shown that the incommensurate structure of $ThBr_4$ must be of higher order than $q_s/c^* = 4/13$.

Introduction

Absorption and emission spectra of U^{4+} diluted in $ThBr_4$ have been reported previously. At room temperature $ThBr_4$ (β form) has a tetragonal crystal structure with each Th atom (or impurity U atom) located at a site of D_{2d} symmetry. At liquid He temperatures, the spectra consisted of many more lines than could be reasonably attributed to zero phonon electronic transitions of a $5f^2$ configuration. Also, no constant differences could be found in the line list to suggest vibrational structure superimposed on electronic transitions. Another puzzling feature of the low temperature optical spectra was the presence of broad absorption bands with two edge singularities in lieu of the sharp lines usually found for an f^n system. The apparently continuous character of fluorescence lines observed in selective excitation experiments suggested the existence of a continuous distribution of U^{4+} sites in the host crystal. The first evidence as to a possible explanation of these observations came from Raman scattering results which indicated the existence of a phase transition, T_c = 95 K, in $ThBr_4$.[2] Subsequently, neutron powder diffraction data showed additional powder lines below T_c, which could be indexed approximately by tripling the unit cell along the c axis.[3] More precise single crystal neutron diffraction measurements indicated that below T_c, $ThBr_4$ has a "displacively modulated structure", i.e. the regular spatial arrangement has been disturbed by small-amplitude static displacements of the atoms with a period incommensurate with the underlying crystalline periodicity.[4]

Delamoye and Currat[5] have shown that the peculiar absorption bands found in the optical spectra of U^{4+}:$ThBr_4$ can be explained by the incommensurate structure of the host crystal at low temperatures. The Th (U impurity) ions are situated at sites which vary continuously from D_{2d} to a limiting D_2 symmetry. In this paper we describe selective excitation experiments which permit the classification of the absorption and emission lines according to site symmetry. The following paper[6] (II) fits the levels of U^{4+} in the D_{2d} and limiting D_2 sites to the parameters of an empirical Hamiltonian.

Energy Levels in the $ThBr_4$ Modulated Structure

Below T_c = 95 K, $ThBr_4$ exists as an incommensurately modulated structure due to transverse sinusoidal displacements of the bromide ions perpendicular to the c axis of the crystal. The bromide ion displacements are different in each unit cell and are a sinusoidal function of the distance from their positions in the high temperature unit cell which is taken as the origin. These displacements may be described in terms of a local phase angle ϕ_ℓ where ℓ is an index which identifies the site. Thus $\phi_\ell = 0$ for the D_{2d} site and $\phi_\ell = \pm \pi/2$ for the limiting D_2 site. For D_{2d} symmetry, the energy levels of an f^2 system may be labelled by the representations of the D_{2d} group as the singlets $\Gamma_1 - \Gamma_4$, and the doublet Γ_5. Although in the modulated structure of $ThBr_4$, the site symmetry is lowered to

D_2, we will use the D_{2d} designation (i.e. Γ_1 (D_{2d})) in the following discussion.

Delamoye and Currat[5] have shown that the energy of the jth energy level of a U^{4+} ion in the ℓth site in the modulated $ThBr_4$ structure may be written as

$$E^j = E_0^j + \eta^2 \{\alpha_j + \beta_j \sin^2 \phi_\ell\} \pm \gamma_j \eta \sin \phi_\ell \qquad (1)$$

where α_j, β_j and γ_j are coefficients, and $\gamma_j = 0$ for the Γ_1 - Γ_4 (D_{2d}) states. η is an amplitude factor which is assumed to be small. At each site ℓ, the possible electronic transition frequencies between two levels j and j' are given by[5]

$$\nu = E_\nu^j - E_\nu^{j'}$$

and the spectral density of the corresponding absorption band by

$$I_\nu^{jj'} = \left| \frac{d\nu^{jj'}}{d\phi_\ell} \right|^{-1} .$$

The edge singularities correspond to

$$\frac{dE_\ell^{(j')}}{d\phi_\ell} = \frac{dE_\ell^{(j)}}{d\phi_\ell} .$$

The resulting energy level diagram is sketched in Fig. 1. When the phase angle $\phi_\ell = 0$, the U^{4+} ion is in a D_{2d} symmetry site.

For other values of ϕ_ℓ the symmetry is D_2 with the limiting D_2 site occurring at $\phi_\ell = \pm \pi/2$. Edge singularities occur at $\phi_\ell = 0, \pm \pi/2$ for non-degenerate ($T>T_c$) excited states and $\phi_\ell = \pm \pi/2$ for the states derived from the D_{2d}-degenerate Γ_5 states.

As ϕ_ℓ goes from 0 to $\pm \pi/2$, the $\Gamma_1 - \Gamma_4$ (D_{2d}) levels are shifted in energy by an amount proportional to the square of the modulation amplitude. The degenerate Γ_5 (D_{2d}) levels are split by the B_2^2, B_2^4, B_2^6, B_6^6 crystal field terms which occur in D_2 symmetry but not in D_{2d} symmetry.[6] In this case the band width is proportional to η.

Thus the narrow π transitions must be between nondegenerate states with energy shifts proportional to η^2, and σ transitions must correspond to those in which at least one of the levels is a Γ_5 (D_{2d}) level with the energy shift proportional to η.

Experimental

A. Equipment

The growth of the U^{4+}:$ThBr_4$ crystals has been described previously.[7] For the studies described here, the crystals were sealed in evacuated quartz tubes containing a small amount of gaseous helium, and then immersed in liquid helium at 4.2 K. The luminescence of the U^{4+} ions was excited by a pulsed Molectron DL tunable dye laser pumped with a Molectron UV14 nitrogen laser. The nitrogen laser generated a pulse of ~ 10 ns width with a peak power of 400 KW at a

repetition rate of 10 Hz. The resolution of the dye laser was ~ .1 nm at 600 nm.[8] Fluorescence spectra were obtained photographically on a 3.4 m Ebert spectrometer or analyzed with a .5 m Jarrell-Ash monochromator equipped with a Hamamatsu 928 photomultiplier. Zeeman spectra were obtained with a magnetic field of 4.2 Tesla oriented parallel to the c crystal axis. All experiments described here were performed in the visible region.

B. Absorption and Broad Band Excitation Spectra

The absorption and broad band excitation spectra are characterized by two distinct types of bands depending upon the polarization of the electric vector of the incident radiation with respect to the c axis. With σ polarization the absorption spectra (Fig. 2a) consist of broad bands with three peaks, two of which are associated with edge singularities. With π polarization the absorption bands (Fig. 2b) are narrower and have two peaks, which are associated with singularities. Broad weak peaks which accompany some bands are probably due to vibronic transitions. If fluorescence spectra are obtained with a broad band excitation source, the fluorescence bands exhibit a characteristic line shape with two edge singularities. A typical band is shown in Fig. 3.

C. Selective Excitation Experiments

If a narrow band dye laser is set to a particular absorption line, only those ions with the site symmetry of the absorbing ion will be excited and show a fluorescence spectrum. If two sites have overlapping absorption lines the fluorescence spectrum will consist of

emission lines from both sites whose relative intensities will be proportional to the relative number of ions from each site which are excited. Part of the fluorescence spectra obtained by the laser excitation of various absorption peaks at ~ 517 nm (see Fig. 2a) is shown in Fig. 4. If an emission line due to U^{4+} ions in a particular site is monitored while the dye laser is scanned through an absorption band, only those absorption lines from ions in the same site will excite the fluorescence. From these types of experiments excitation spectra can be determined and the absorption and emission lines can be correlated.

The lines observed for U^{4+}:$ThBr_4$ have been assigned to three different sites: A,B, and C. These sites are sufficient to classify all the major features of the absorption and emission spectra. Table I lists the wavelengths and energies for the absorption and emission spectra associated with the edge singularities (in both π and σ polarization) and also the third peak in the σ polarization spectra (See Figs 2 and 3). These spectra are labelled as arising from the A and B sites. Later experiments showed the intensities of some of these lines to be temperature dependent.[9]

Excitation spectra obtained by monitoring emission lines between 544.1 and 545.5 nm are shown in Fig. 5. The absorption intensity between the edge singularities and the third peak (see Fig. 2a1) corresponds to many different sites. This range of sites results in an emission spectrum which appears to vary continuously as the exciting laser frequency is tuned through an absorption band.

Examples of this effect, obtained by sweeping through the absorption band of Fig. 2a1, are shown in Fig. 6. The data shown in Fig. 6b were obtained from the experiments illustrated in Fig. 5. Similar data obtained by excitation of the absorption band at ~ 576 nm (Fig. 2a2) are shown in Fig. 7. It has not been possible to resolve fluorescence or excitation spectra from an individual site. The family of lines arising from the excitation of an absorption band between the edge singularities and, in the case of σ polarization, the third peak in the spectrum, have been assigned to the multiple C sites.

From Zeeman measurements it was found that two visible absorption lines assigned to the B site were split into doublets. The splittings were linear with the magnetic field strength. Values of the splitting factor are given in the following paper (II).

Discussion

The selective excitation experiments show that one of the two singularities (A site) in the π polarization spectra is associated with two edge singularities in the σ polarization spectra, while the third peak in the σ polarization spectra (B site) is correlated with the second singularity in the π spectra. From the arguments of Delamoye and Currat,[5] the B site is assigned to the site of D_{2d} symmetry while the A site represents the limiting D_2 site symmetry found for the modulated phase of $ThBr_4$. Implicit in these arguments is the assignment of the ground state to a singlet in D_{2d} symmetry. This assignment is supported by the number of absorption lines found

for the D_{2d} symmetry site; if a degenerate Γ_5 state were the ground state, the selection rules would be much different (see II) and many more lines would be observed with π polarization. Also Zeeman experiments show only a splitting of the excited Γ_5 (D_{2d}) states; no splittings due to a degenerate ground state are observed.

The energy transfer by non-radiative transitions is strongly dependent on the energy difference between the absorbing level and the fluorescing level as shown by the relative intensities in Table I. For example, for the A site, the line at 14354 cm^{-1} is weak when excited at 516.6 nm but is strong when excited at 576.3 nm. Because the line at 14354 cm^{-1} is also seen in absorption but is temperature dependent we conclude that there is an excited state at 10 cm^{-1} for the A site. This 10 cm^{-1} level is verified by the energy difference of the emission lines at 19302 and 19292 cm^{-1} and the temperature dependence in absorption of the latter. From this group of lines we also find levels at 146 cm^{-1}, 967 cm^{-1} and 1010 cm^{-1} for the A site. The temperature dependence of the line at 16996 cm^{-1} in absorption suggests that it arises from the level at 10 cm^{-1} and permits us to assign a level at 17006 cm^{-1}. The levels determined by this analysis and the visible absorption lines are shown in Table II.[10]

Only two lines are seen in both absorption and emission for the B sites and locate levels at 15206 and 14368 cm^{-1}. The emission line at 14290 cm^{-1} fixes an excited state at 78 cm^{-1}. The selective excitation experiments show that the 78 cm^{-1} line is split into a

doublet in D_2 symmetry (see Fig. 6) so it must be of Γ_5 symmetry. We assign the termination of the emission lines at 16919 and 19233 cm^{-1} to this state which locates levels at 16997 and 19311 cm^{-1}. The emission line at 18364 cm^{-1} is excited by the same absorption line as the 19233 cm^{-1} line and locates an excited state at 943 cm^{-1}. The assigned levels for the visible region obtained from both absorption and emission experiments for the B site are also shown in Table II.

According to the line shape analysis of Delamoye and Currat,[5] the A sites correspond to the phase angle of $\phi_\ell = \pm \pi/2$ while at the B or D_{2d} site, $\phi_\ell = 0$. For a particular band the measured energies at these sites permit the empirical evaluation of the coefficients in Eq. 1. This equation can then be used to map out the energy levels as a function of the phase angle ϕ_ℓ. Fig. 8 shows some of these energy levels. All levels have been measured relative to the ground state and consequently the energy levels obtained from Eq. 1 as a function of the modulation or phase angle ϕ_ℓ are given relative to the ground state. Three of the levels shown are Γ_5 states in D_{2d} symmetry. The two higher Γ_5 states are obtained from absorption measurements and the profiles of the absorption bands are sketched in Fig. 8. Note that in one case the absorption from a B (D_{2d}) site arises at an edge singularity while for the highest energy level the absorption from a B site is found between the two edge singularities. The energy levels as a function of phase angle are quite different in the two cases. Two states which are singlets in D_{2d} symmetry are also

shown. In these cases the energy shifts in going from D_{2d} to the limiting D_2 site are not so pronounced. This is the reason for the rather narrow absorption bands found in π polarization.

The validity of Eq. 1 can be checked by determining the phase angle at a particular absorption frequency and then calculating the fluorescence energy predicted from the difference of two energy levels which are pumped via the absorption band at that phase angle. By this type of analysis the fluorescence energies of the U^{4+} ions at various C sites should be determined. The calculated fluorescence energies for some bands are shown as dashed lines on Fig 6C and 7B. The agreement is seen to be remarkably good and within experimental error.

Neutron diffraction experiments indicate a modulated structure with a modulation wavevector q_s given by

$$q_s = 0.310 \pm 0.005\ c^*$$

where c* is one of the basis vectors of the reciprocal lattice of the tetragonal unit cell. A high order commensurate structure corresponding to

$$\frac{q_s}{c^*} = 4/13 = 0.3077 \qquad \text{or} \qquad \frac{q_s}{c^*} = 5/16 = 0.3125$$

cannot be excluded on the basis of neutron diffraction measurements alone.

However, we have shown by the selective excitation experiments

(see Figs 5 and 6) that it is impossible to resolve emission lines from an isolated C site. The two edge singularities (516.6 and 517.6 nm) are separated by 34 cm^{-1}. The resolution of the dye laser was ~ 2 cm^{-1} which shows there must be $\geq$ 17 different U^{4+} (or Th^{4+}) sites. If $ThBr_4$ does have a high order commensurate structure, it must be of a higher order than $q_s/c^* = 4/13$.

Conclusion

The observation of peculiar line shapes found for absorption spectra of U^{4+}:$ThBr_4$ and of fluorescence lines which shift continuously as the exciting laser frequency is swept through the profile of an absorption band have led to the discovery of the incommensurate phase of $ThBr_4$ at T_c = 95 K. Selective excitation experiments have permitted the correlation of absorption and emission lines with the site symmetry of the U^{4+} ion in $ThBr_4$. The lines have been classified as arising from a D_{2d} (B) site with a continuous distribution of sites (C) to the limiting D_2 (A) site and energy levels as a function of the phase angle have been mapped. This continuous distribution of sites explains the unusual fluorescence behavior. Our experiments have shown that a high order commensurate structure of $q_s/c^* = 4/13$ is not possible. A higher resolution laser is necessary to determine if a higher order commensurate phase exists for $ThBr_4$.

Acknowledgements

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References

1. M. Genet, P. Delamoye, N. Edelstein, and J. Conway, J. Chem. PHys. 67, 1620 (1977).

2. S. Hubert, P. Delamoye, S. Lefrant, M. Lepostollec, and M. Hussonnois, J. Solid State Chem. 36, 36 (1981).

3. R. de Kouchkovsky, M.F. LeCloarec, and P. Delamoye, Mater. Res. Bull. 16, 1421 (1981).

4. L. Bernard, R. Currat, P. Delamoye, C.M.E. Zeyen, S. Hubert, and R. deKouchkovsky, J. Phys. C: Solid State Phys. 16, 433 (1983).

5. P. Delamoye and R. Currat, J. Physique Lettres 43, L655 (1982).

6. P. Delamoye, K. Rajnak, M. Genet, and N. Edelstein, Phys Rev. B, following paper.

7. M. Hussonnois, J.C. Krupa, M. Genet, L. Brillard, and R. Carlier, J. Crystal Growth 51, 11 (1981).

8. The dyes used in these experiments were 7D4MC, 7D4TMC, Coumarin 500, and Rhodamine 6G. They were obtained from the Molectron Corporation.

9. B. Briat, P. Delamoye, J.C. Rivoal, S. Hubert, and P. Eveque, to be published.

10. The lines and levels listed in Tables I and II are, in some instances, different than those tabulated in Ref. 1. Ref. 1 assumed the centers of the broad bands should be taken as the level. The subsequent line shape analysis (Ref. 5) showed this assumption was not correct.

Table I.

Absorption and Emission Lines Assigned to the A and B Sites

A sites						B sites					
Excitation[a]			Emission[a]			Excitation[a]			Emission[a]		
nm	cm^{-1}	Polarization	nm	cm^{-1}	Intensity[b]	nm	cm^{-1}	Polarization	nm	cm^{-1}	Intensity[b]
457.8	21838	σ	518.2[c]	19292	s	457.7	21842	σ	519.8	19233	s
			545.3	18333	m				544.4	18364	s
			546.5	18293	w						
488.5	20460	π	518.2[c]	19292	s	488.5	20460	π	519.8	19233	s
			545.3	18333	m				544.4	18364	s
			546.5	18293	w						
						490.4	20382	σ	519.8	19233	m
516.6	19352	σ	518.0[d]	19302	vw						
			518.2[c]	19292	vs						
			522.0	19154	w						
			545.3	18333	m						
			546.5	18293	w						
			657.4[d]	15207	m						
			696.5[c]	14354	w						
517.5	19318	σ	518.0[d]	19302	vw	516.9	19341	σ	519.8	19283	s
			518.2[c]	19292	vs				544.4	18364	s
			522.0	19154	w				657.5[d]	15204	m
			545.3	18333	m				699.6	14290	w
			546.5	18293	w						
			657.4[d]	15207	m						
			696.5[c]	14354	w						
518.0	19302	σ	545.3	18333	m						
			546.5	18293	w						
			657.4[d]	15207	m						
			696.5[c]	14354	w						
575.6	17368	σ	588.2	16996	m						
			696.0[d]	14364	w						
			696.5[c]	14354	s	576.7	17335	σ	590.9	16919	m
									695.8[d]	14368	w
576.3	17347	σ	588.2	16996	m				699.6	14290	s
			696.0[d]	14364	w						
			696.5[c]	14354	s						
670.3	14915	π	696.5[c]	14354	m	671.0	14899	π	699.6	14290	m
679.7	14709	σ	696.5[c]	14354	m						
684.2	14612	σ	696.5[c]	14354	m	682.2	14654	σ	699.6	14290	m

[a]Estimated Errors ± 2 cm^{-1}.

[b]s = strong, m = medium, w = weak, vs = very strong, vw = very weak.

[c]Seen also in absorption but temperature dependent.

[d]Seen also in absorption.

Table II.

Energy Levels Assigned to the A and B Sites

A sites		B sites	
Energy (cm^{-1})	Polarization	Energy (cm^{-1})	Polarization
22220[a]	σ	22220[a]	σ
21838	σ	21842	σ
20460	π	20460	π
		20382	σ
19942[a]	σ	19970[a]	σ
19352	σ	19341	σ
19318	σ		
19302	π	19311	π
17368	σ	17335[b]	σ
17347	σ		
17006		16997	
16013[a]	σ	16003[a,b]	σ
16003[a]	σ		
15421[a]	σ	15412[a]	σ
15392[a]	σ		
15207	π	15204	π
14915	π	14899	π
14709	σ	14654	σ
14612	σ		
14364	π	14368	π
1010		943	
967			
146		78	
10			
0		0	

[a]Determined from MCD experiments, see Ref. 9.
[b]These levels split in a magnetic field.

Figure Captions

Figure 1. Energy level diagram obtained from Eq. 1: a) singlet state $\beta > 0$, b) doublet state $\beta > 0$, c) singlet state $\beta < 0$.

Figure 2. Typical absorption bands in a) σ polarization, b) π polarization.

Figure 3. Typical emission band obtained by broad band excitation.

Figure 4. Fluorescence spectra obtained by pumping various absorption peaks at ~ 517 nm; (See Fig. 2a1). Laser wavelength set at a) 516.6 nm, b) 516.9 nm, c) 517.5 nm.

Figure 5. Excitation spectra obtained by monitoring various wavelengths in the 544–545 nm region. The absorption band being swept by the narrow band dye laser is centered at 517 nm and is shown in Fig. 2a1.

Figure 6. Change in fluorescence energies as the absorption band at ~ 517 nm (19337 cm^{-1}) is swept by the narrow band dye laser: Emission band at 6a) ~ 19210 cm^{-1}, 6b) ~ 18350 cm^{-1}, 6c) ~ 14310 cm^{-1}. The horizontal lines represent the band widths at particular monochromator settings.

Figure 7. Change in fluorescence energies as the absorption band at ~ 696 nm (14364 cm^{-1}) is swept by the dye laser: Emission band at 7a) ~ 16960 cm^{-1}, 7b) ~ 14320 cm^{-1}. The horizontal lines represent the band widths at particular monochromator settings.

Figure 8. Energy levels obtained as a function of ϕ_ℓ by fitting the parameters of Eq. 1 to the measured energies at the A and B sites. The levels are relative to the energy level of the ground state which is assumed to be 0 cm^{-1}. The dashed lines represent the profiles of the absorption bands from which the parameters were evaluated. The energy levels at ~ 19340 cm^{-1}, ~ 17340 cm^{-1}, and ~ 80 cm^{-1} arise from Γ_5 doublets in D_{2d} symmetry while the levels at ~ 19310 cm^{-1} and 14360 cm^{-1} are singlets in both D_{2d} and D_2 symmetries.

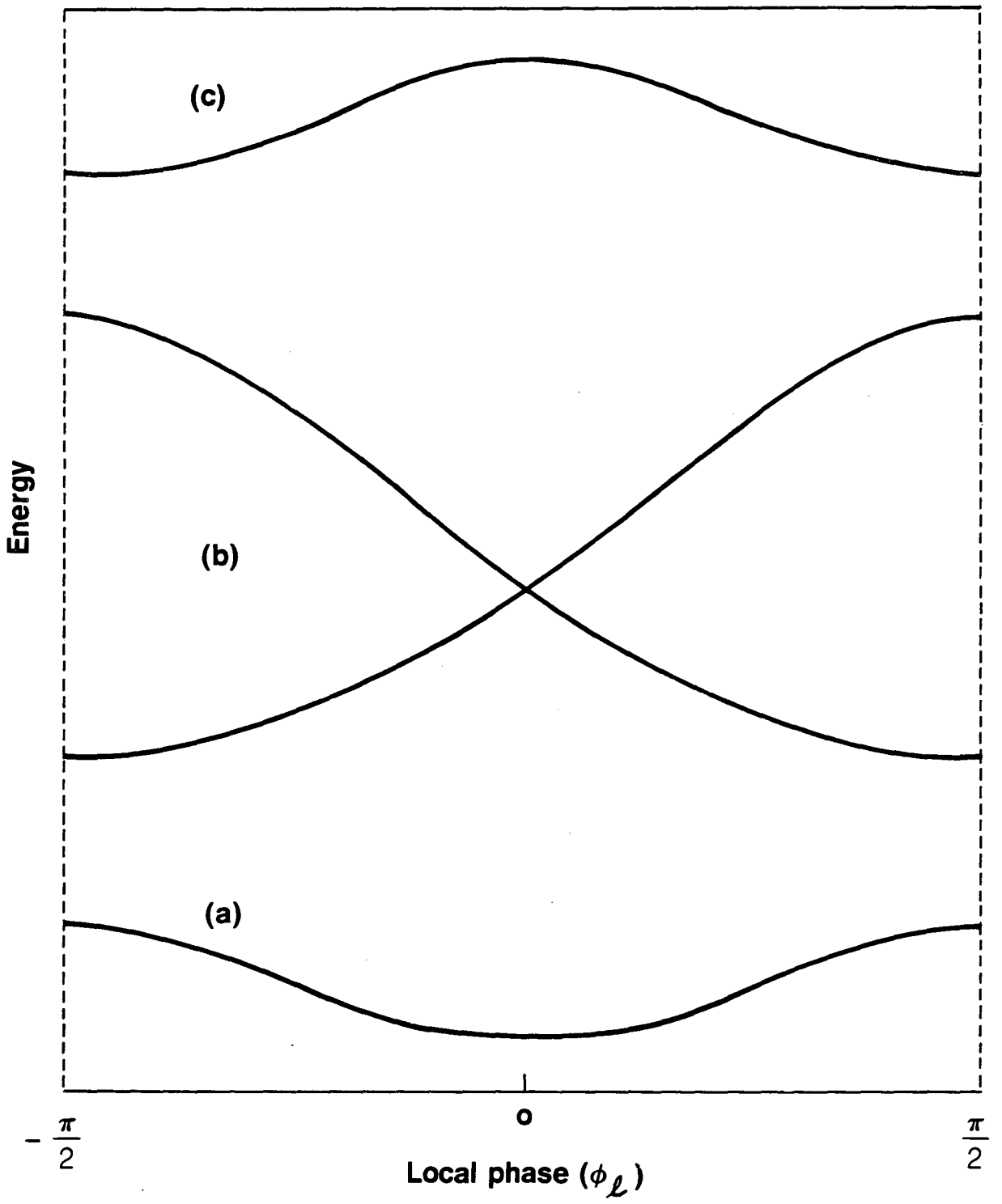

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Figure 1

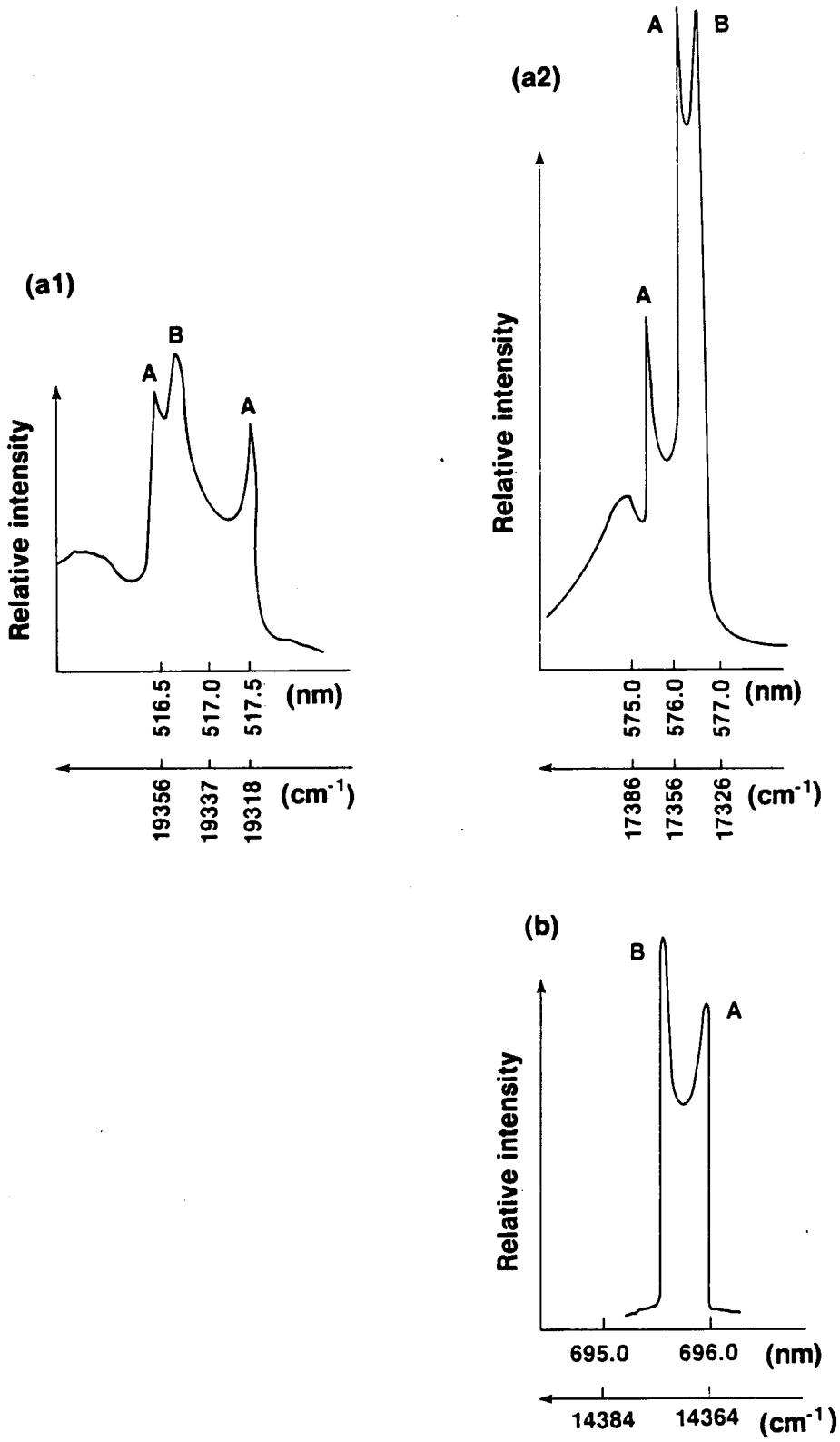

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Figure 2

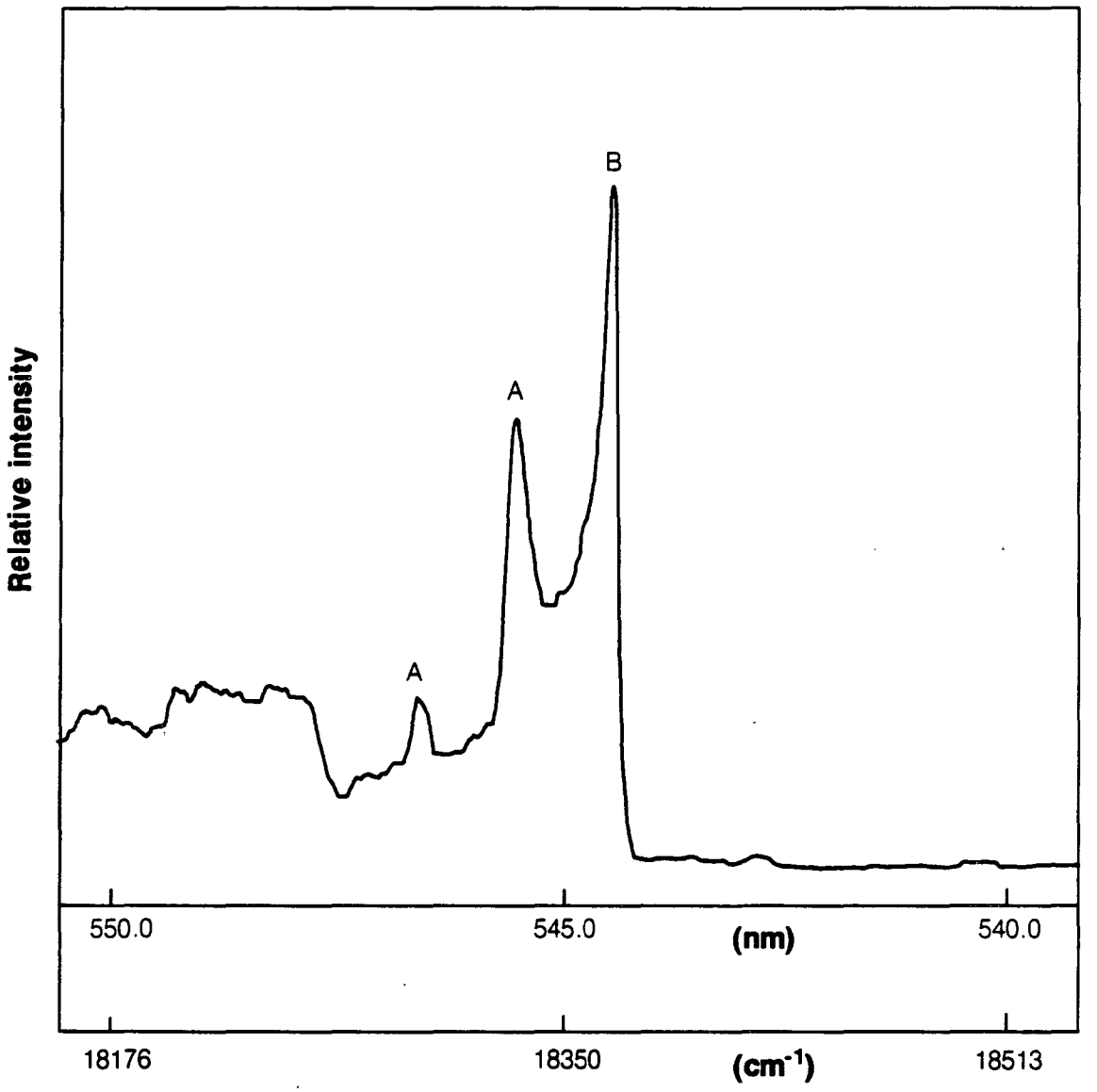

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Figure 3

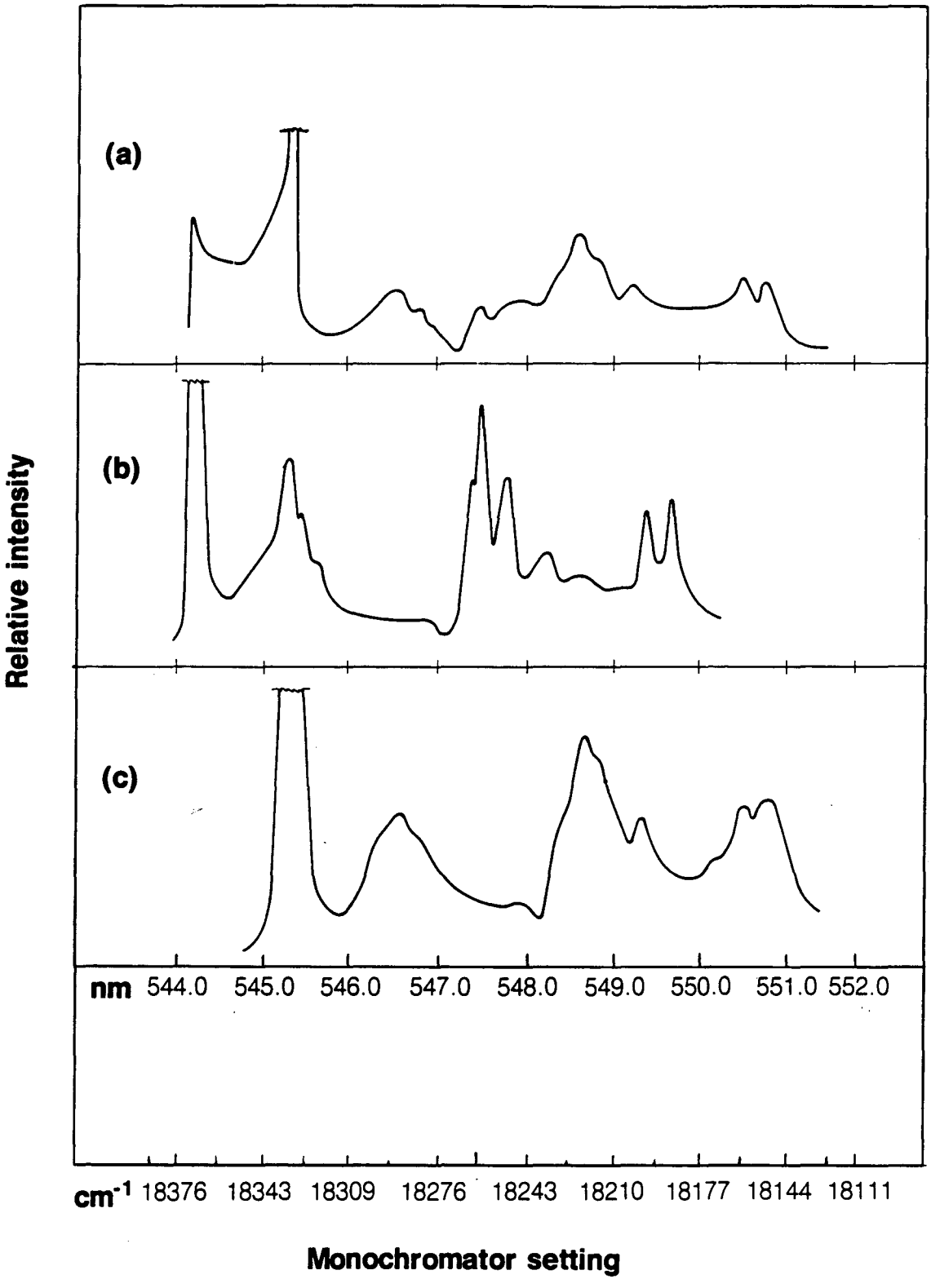

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Figure 4

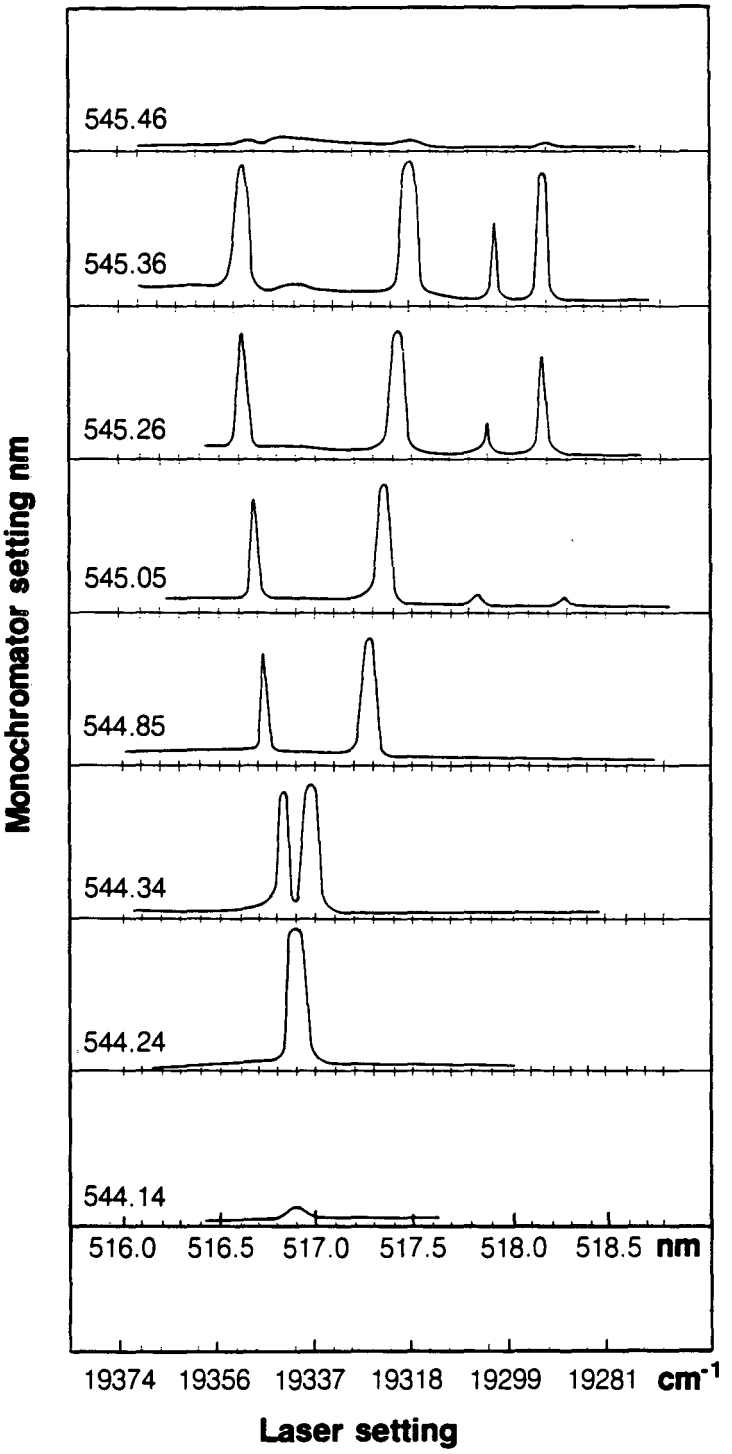

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Figure 5

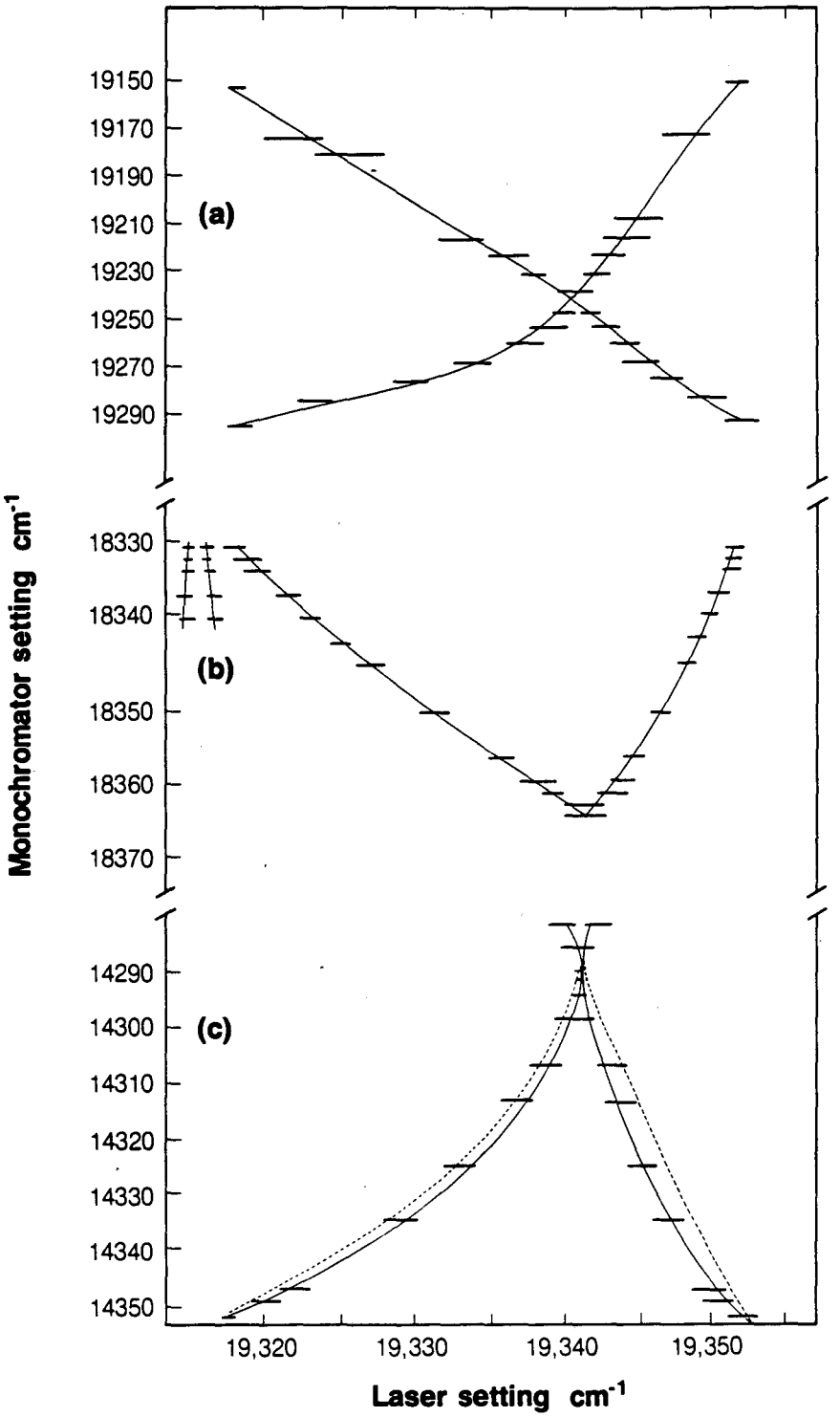

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Figure 6

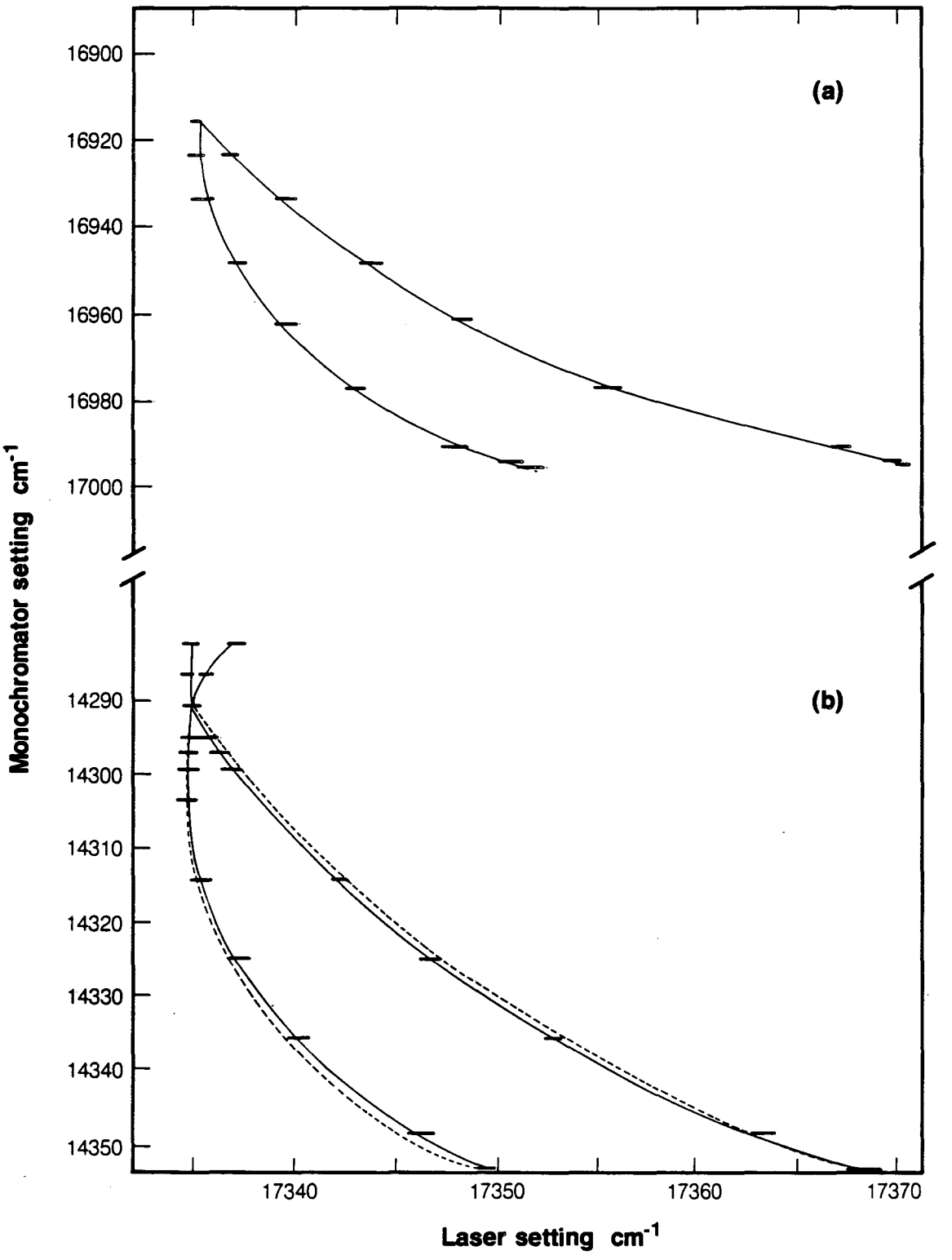

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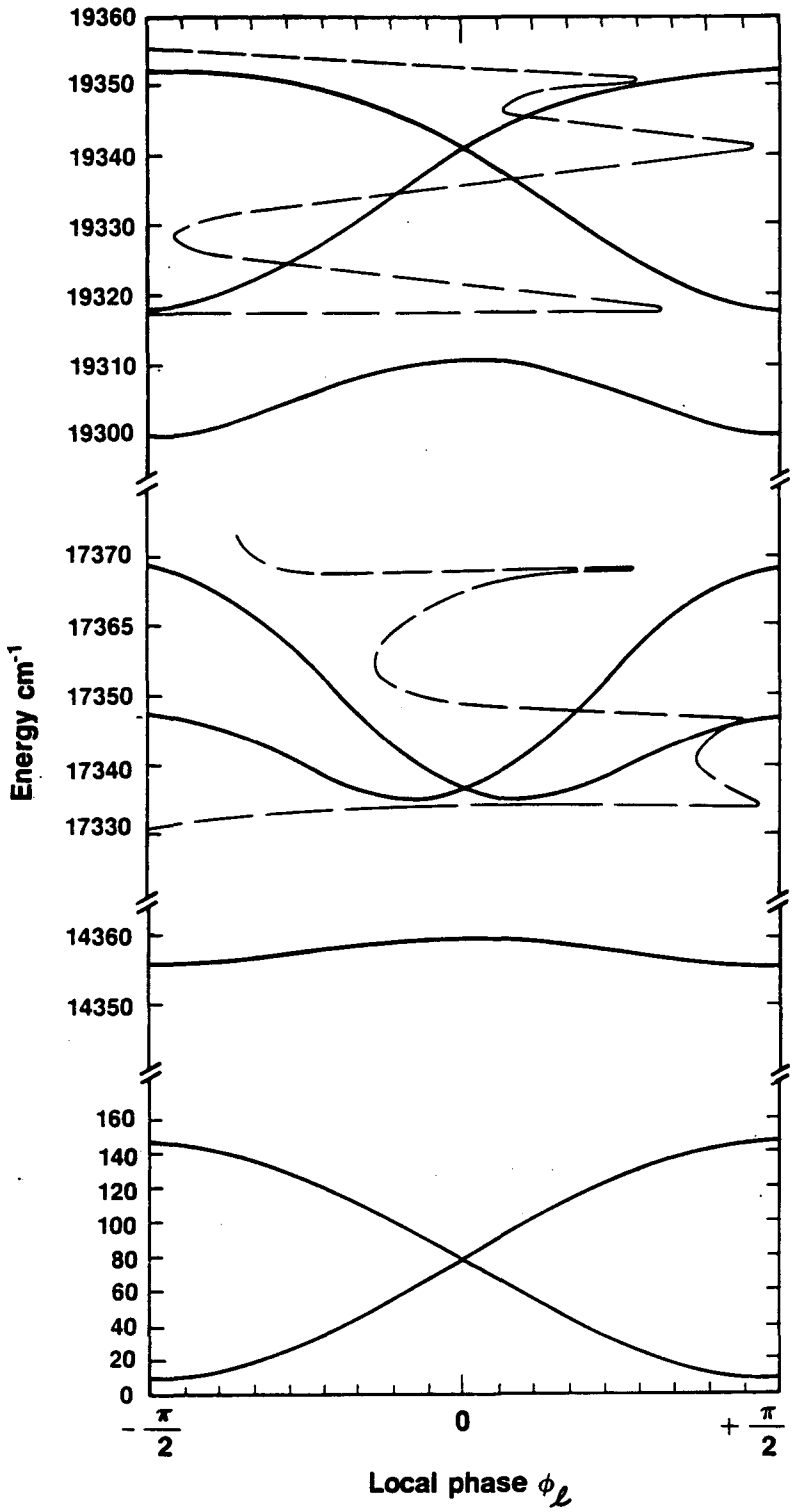
Figure 7



XBL 837-10528

Figure 8

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