# REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE
1995

3. REPORT TYPE AND DATES COVERED
Interim

4. TITLE AND SUBTITLE
On the Jahn-Teller Effect of $Mn^{2+}$ in Zinc-Blende ZnS Crystal

5. FUNDING NUMBERS
N00014-90-J-1608
G

6. AUTHOR(S)
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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
Chemistry Division Code 1113
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
Technical Report 29

11. SUPPLEMENTARY NOTES
J. Chem. Phys., Published (1994) **102**, 34-38.

12a. DISTRIBUTION/AVAILABILITY STATEMENT
This document has been approved for public release: its distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

See attached Abstract.

DTIC
SELECTED
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S D
B

19950427 005

DTIC QUALITY INSPECTED 5

14. SUBJECT TERMS

15. NUMBER OF PAGES
24

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
Unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT
Unclassified

20. LIMITATION OF ABSTRACT
SAR

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102

OFFICE OF NAVAL RESEARCH

GRANT or CONTRACT N00014-90-J-1608

R&T CODE 4131057- - - 01

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Prepared for Publication or Published

in the

J. Chem. Phys.

University of Florida
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April 18, 1995

# On the Jahn-Teller Effect of $Mn^{2+}$ in Zinc-Blende ZnS Crystal

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## Abstract

The excited states of $Mn^{2+}$ in zinc-blende ZnS crystal have been studied by the Intermediate Neglect of Differential Overlap model parametrized for spectroscopy (INDO/S) within the Restricted Open-Shell Hatree-Fock (ROHF)-Configuration Interaction (CI) approximation. The effect of the Jahn-Teller (JT) active *e*-mode on the first excited state ($a^4T_1$) has been examined with respect to energy barriers and geometric distortions. The dynamical JT effect has been studied and the excited state absorption (ESA) profiles for different *e*-mode conformations have been calculated. Good reproduction of the experimental ESA spectrum has been obtained for nuclear arrangements corresponding to small S-Mn-S angle distortions. The off-center $\tau_2$-mode vibrations were found to promote the JT coupling by reducing the barriers between the stable structures.

# I. INTRODUCTION

The excited states of $Mn^{2+}$ ion in cubic ZnS have been extensively studied both theoretically and experimentally.[1-5] Special attention has been paid to the Jahn-Teller (JT) effect that takes place in the low-energy degenerate quartet excited states, and especially the lowest excited $a^4T_1$ state that heavily influences the absorption and emission properties of ZnS:Mn.[6-8] The transitions from and to the ground state, $^6A_1 \leftrightarrow a^4T_1$, are spin and symmetry forbidden within $T_d$, so that coupling with asymmetric vibrational modes is believed to be the principal source of the intensity of the bands experimentally observed. Additionally, the long-lived $a^4T_1$ state provides the opportunity to perform excited state absorption (ESA) experiments, a technique that has proved successful in ZnS:Mn spectroscopy.[9,10] Several peaks have been observed in the visible region, the most intensive at 1.49 and 1.90 eV, but their origin has not yet been clarified. Typically, such an assignment would require a knowledge of the reference excited state geometry, a question that poses another: what is the extent of the JT distortion which results from coupling with the JT active *e*-modes and reduces the initial tetrahedral geometry into $D_{2d}$ ?

In previous papers[11,12] semiempirical methods have been used to elucidate problems relating to the JT effect of $Mn^{2+}$ in Group II-VI compounds. In this work we apply the Intermediate Neglect of Differential Overlap model parametrized for spectroscopy (INDO/S) within the Restricted Open-Shell Hartree-Fock (ROHF) approximation to the excited states of $Mn^{2+}$ in ZnS, and follow these calculations with a Configuration Interaction (CI) treatment. The aim of this study is *(i)* to see how well this model reproduces the spectroscopic features of the above system, *(ii)* to reexamine the JT effect taking place for the first excited state of ZnS:Mn, and *(iii)* to relate the calculated properties to the experimental ESA spectra. For these studies we will use the INDO model[13–16] implemented in the program ZINDO.[14–16] This model has been used successfully to study JT effects in transition-metal complexes[17] and in small clusters.[18–20]

## II. METHOD AND MODEL

In this work we have adopted a model that reflects the experimental zinc-blende ZnS:Mn structure: a tetrahedral $MnS_4$ cluster with Mn-S bond length 2.35 Å. As shown in previous studies,[4,12] the inclusion of the surrounding lattice is necessary to correctly assess the transition energies[4] and the JT splittings.[12] Toward this end, we have considered an external potential modeled by 12 point charges, each having +0.5 charge, situated at the crystallographic positions corresponding to Zn lattice sites in ZnS - 3.82 Å away from the central $Mn^{2+}$ ion. The addition of 12 point charges creates a neutral cluster of overall $T_d$ symmetry and forms an external potential that simulates the rest of the lattice. As shown below, this model reproduces well the absorption spectroscopy of the ground state, when the Franck-Condon principle is active. The excited state spectrum, however, is from a JT distorted structure in which the lattice charges have been hold fixed in their ground state positions. There is no easy way to allow geometric relaxation of the lattice within this model. We believe that the latter effect is small as (1) the neighbors of the cluster represented by point charges are bound to three other lattice atoms helping to anchor their positions, and (2) the JT distortions, themselves, are presumably small. We recognize, however, that our calculated distortions under this model might be underestimated. Although the calculated energy of the JT distorted cluster might be too high in the absence of lattice relaxation, it is difficult to translate this error into errors of transition energies from the distorted first excited state to the other higher lying states. An estimate of 0.08-0.10 eV for the lattice relaxation of the first excited state can be made assuming a model suggested earlier[12] that considers second neighbor correlated motion. These values are obtained for small second neighbor displacements , typically 0.005 Å, and angle distortions up to ±20° produced by the JT active *e*- mode.[12] Some of the higher excited states that are reached from the first excited state (ESA) might be similarly distorted, and the errors cancel, others might not distort or distort along a different symmetry, leading us to underestimated transition energies. In this latter case, the maximum error might be estimated at 0.16-0.20 eV These effects are small, at least with respect to the errors introduced in this model, and in the computation.

Spectroscopic INDO parameters have been used here as originally parametrized.[14,15] Extensive configuration interaction (CI) calculations have been carried out that include all CI single (CIS) excitations. At this level of approximation we hope to have taken into account all important contributions coming from d-d and s,p-d transitions. Since the ground state ($^6A_1$) and the quartet excited states differ in spin multiplicity, they have been calculated separately and the identification of the excited states was based on energy and transition moments and their splitting patterns upon reduced symmetry.

All states have been thoroughly checked with respect to configuration origin: $^6A_1$ ($e^2t_2^3$); $^4T_{1,2}$ ($e^1t_2^4$, $e^2t_2^3$, $e^3t_2^2$); $^4E$, $^4A_1$, $^4A_2$ ($e^2t_2^3$). Additionally, the transition energy to the lowest doublet state $a^2T_2$ has been calculated, a state stemming from 10 possible $e^xt_2^{5-x}$ configurations with x ranging from 0 to 4, and all contributing slightly to the ZnS:Mn spectrum due to their double spin-flip origin. We note that two of the configuration involved in this state ($e^4t_2^1$ and $t_2^5$) arise from double excitations from the ground state configuration ($e^2t_2^3$) and their inclusion requires another type of CI (CI singles and doubles) so that the calculated state energy cannot be directly compared with that of the quartet excited states. This difference, however, appears to be of marginal importance as the $a^2T_2$ state is calculated usually much higher in energy than that of the first excited state.[4,5]

Two major types of JT normal modes have been experimentally detected:[6,7]

(*i*) the *e*-mode involving a pure bending vibration of the S-Mn-S angles and preserving the $S_1$-Mn-$S_2$/$S_3$-Mn-$S_4$ dihedral angle the same as in the original $T_d$ structure (90°). The initial $T_d$ symmetry of the impurity center is reduced by the *e*-mode to $D_{2d}$.

(*ii*) the $\tau_2$-mode that can be modeled by off-center movement of the central metal atom towards one of the ligands. This mode is predominantly a stretching one and reduces the tetrahedral environment to $C_{3v}$. The $\tau_2$-modes were found both theoretically and experimentally to be an order of magnitude less active than the normal *e*-mode.[7]

The above two modes do not mix through the vibronic Hamiltonian under $T_d$ symmetry. However, their products can transform into each other at reduced symmetries: Table 1 shows the term splittings that are observed for structures symmetries lower than $T_d$. As seen from Table 1, the first excited $^4T_1$ state can be brought into JT minimum either through an *e*-mode and a subsequent $^4$E splitting to $^4$B$_1$ and $^4$B$_2$ in $C_{2v}$, or by an off-center $Mn^{2+}$ movement that reduces the symmetry to $C_{3v}$, followed by further coupling with a normal mode that reduces the symmetry to $C_{2v}$. This latter vibration is a third mode under consideration in this work: the bending *e*-mode of the $C_{3v}$ group that distorts the structure to $C_{2v}$. This mode is nearly the same as in $T_d$, with the only difference that it takes place at unequal Mn-S bond lengths.[21] The resulting geometries can easily be converted to $D_{2d}$ by simply having the central atom relax back to its original position.

The JT distortions considered above may occur only if the excited state under consideration is long enough lived to provide the necessary time for the nuclear relaxations. As already mentioned, we concentrate here exclusively on the stabilization of the first excited state $a^4T_1$, a state which is spin and symmetry forbidden in $T_d$, and is therefore expected to be long lived . Higher energy states are of minor importance for this work for they are likely to internally convert or intersystem cross to either this state or ground state. The lowest excited state is observed to be populated in the ESA experiments.[9,10]

The predominantly manganese 3*d*-orbitals have been carefully monitored during the mode simulations in order to avoid state mixings. Typically, the energy ordering of the *d*-orbitals was in accordance with the theoretical predictions for the above symmetries. Only at very large angle or bond length distortions, is a reordering of the *d*-orbitals observed due to the higher repulsion, but these structures are of no practical importance as they reflect extreme geometries that are not physically reachable under normal conditions.

The JT theorem proves that states of non-linear molecules that are spatially degenerate, will distort to a lower symmetry that will destroy the spatial degeneracy, i.e. there is at higher symmetry always a normal mode that will reduce the symmetry. The isolated $MnS_4^{6-}$ center in the excited $a^4T_1$ state would normally distort. The presence of the ZnS lattice, however, may alter the dynamics of this system somewhat and either prevent the distortion or introduce a barrier. We will see that the latter is the case for a simple point-charge model of the lattice.

## III. RESULTS AND DISCUSSION

The method and model described in the previous section have been used to examine the absorption spectrum of ZnS:Mn in its ground state ($T_d$) geometry. The results are summarized in Table 2 where they compared with the *ab initio* calculations of Janssen and Richardson.[4]

The INDO/S calculations give qualitatively the same results as do the *ab initio* calculations; they are in somewhat better agreement with experiment. The assignment of the first 3 bands is in agreement with that generally accepted. Ambiguity exists in the literature on the relative position of the $a^4E$ and $^4A_1$ states originating from the same configurations, some authors calculating $a^4E$ above $^4A_1$,[4] others predicting the reverse ordering.[3,22] Our calculations yield the $^4A_1$ state 100 $cm^{-1}$ higher in energy than the $a^4E$ term.

The assignment of the higher lying quartet states is in line with that given elsewhere.[4,5] The fourth and fifth absorption bands, in increasing energy, are still controversial (see Ref. 4 and references therein) due to the large mixing of states in this energy region. The location of doublet states ($a^2T_2$) and the possible influence of this state on the observed spectrum as suggested earlier[5] is in doubt. On the basis of these calculations, this state is high in energy (3.83 eV) and is expected to have very low intensity due to the spin selection rules. We suggest that it has little influence on the ZnS:Mn spectroscopy.

The electron distribution for the model $MnS_4^{6-}$ ground state was found to be close to that of the ionic case: $3d^{5.06}(e^{2.02}t_2^{3.04})\ 4s^{0.68}\ 4p^{1.15}$ according to the Mulliken population analysis. Since the Mn $4s$ and $4p$ orbitals have their maxima within the ligand region, they can be considered practically depopulated[4] and the total charge on the central Mn atom estimated +1.94. A similar result was obtained from the *ab initio* calculation which yielded a +2.02 charge on the Mn atom.[4] However for these calculations the Mn-S bond distance was set equal to that in cubic MnS, 2.43 Å, as opposed to that used here, 2.35 Å. The long distances might be expected to lead to greater ionic character.

In order to estimate the JT distortions, motion along the asymmetric *e*-mode was examined. Both ground and first excited state energies have been calculated as a function of the bending S-Mn-S angles. Only the lowest component of the $a^4T_1$ state is shown in Figure 1a. Higher energy terms mix to a larger extent as the distortion progresses, and these are of minor importance for the present study as already mentioned.

The two curves shown in Figure 1a can be used to quantify the JT effect for the $Mn^{2+}$ impurity center in the ground and excited states. A large asymmetry of the potential curve exists for the $^6A_1$ ground state due to the inequivalency of the compressed and elongated $D_{2d}$ forms. The $^6A_1$ term has a minimum at the tetrahedral structure in agreement with experiment. The theoretical maximum lies at S-Mn-S angle equal to 180° corresponding to

$D_{4h}$ symmetry. We should to note, however, that such extreme structures are improbable since the surrounding lattice would hinder them, as previously discussed elsewhere.[12] For this reason, we constrain the presentation of our results in Figure 1a to angle distortions of ±40° although these limits might also be considered too great.

The excited $a^4T_1$ state shows stabilization with the $T_d$ *e*-mode in accordance with previous theoretical and experimental studies.[2,4,6,7] The left part of Figure 1a corresponds to elongated $D_{2d}$ forms (S-Mn-S angles smaller than in $T_d$) for which the lowest split state is the $^4E$ term. No stabilization has been observed in this case, as determined previously.[12] A slight minimum can be seen at the $T_d$ geometry for which the $a^4T_1$ term is of lowest energy. This minimum must result from the lattice model that we are using and not allowing the cluster to distort. The JT theorem dictates a distortion from $T_d$ symmetry. Further compression of the cluster brings the system into a new flat minimum with S-Mn-S angle of 138° (29° distortion) and then into a slightly deeper energy region that smooths around the $D_{4h}$ structure. For the compressed $D_{2d}$ form, the $^4A_2$ state was found to be of lower energy and its energy profile strongly supports the experimental findings on the dynamical JT behavior.[6,7] The favorable $D_{2d}$ distortion should pass through a maximum of approximately 650 $cm^{-1}$ (see Figure 1b) at an S-Mn-S angle of 114°, and then the potential curve flattens smoothly.

At the same time, the off-center $\tau_2$-mode, which distorts the $T_d$ to $C_{3v}$, brings about no substantial stabilization of the first excited state (see Figure 1c), the $^4E$ and $^4A_2$ in $C_{3v}$ interchanging their relative positions depending on the direction of the distortion. Two shallow minima of approximately 3 $cm^{-1}$ have been detected for very small distortions corresponding to off-center displacements of ±0.01 Å. This result is in agreement with the experimental and theoretical findings[6,7,11] showing that the JT splittings due to the $\tau_2$-mode are negligibly small compared to that produced by the *e*-mode. As seen from Figure 1c, this mode *alone* is of marginal importance for the excited states and the electron transitions in ZnS:Mn. Combined with the $C_{3v}$ bending *e*-vibration, however, it produces the same stabilization effect as that shown in Figure 1a. Such a mode combination may be possible due to the fact that both $\tau_2$- and *e*-modes in $T_d$ lead to a $^4E$ product that is also subject to JT distortion.

The JT barriers for the combined distortion are considerably lower than that observed for the $T_d$ *e*-mode alone: the 650 cm$^{-1}$ barrier shown in Figure 1b is reduced to 350 cm$^{-1}$. As mentioned before, the $C_{3v}$ and $D_{2d}$ forms may interconvert through $C_{2v}$ provided there is time enough for the nuclear motion. Since the lowest $a^4T_1$ component for the compressed $D_{2d}$ form (S-Mn-S angles larger than in $T_d$) is always the $^4A_2$ state and the latter term is symmetry forbidden for all the symmetries present, this requirement is likely fulfilled. The energy barriers thus observed are easy to overcome at ambient temperatures and facilitate the dynamical JT effect for the excited state. It must also be recalled that any relaxation of the lattice should also lower this barrier. The conclusion that can be drawn from the above considerations is that the *e*-mode conformations can be reached either by direct distortion or through a sequence of asymmetric modes that has sufficiently lower barriers.

We proceed further with the calculation of excited state absorption (ESA) spectra[9,10] arising from excitations from the first excited state to the higher lying states. Such a calculation is unique in the sense that it can provide direct theoretical evidence on the existence, extent and type of the JT distortions taking place in the ZnS:Mn excited states.

The computational scheme we have used was the following: *(i)* calculation of the quartet excited states by INDO/S method within the ROHF self-consistent field (SCF) approximation at CIS level; *(ii)* calculation of the the oscilator strengths for the transitions from the first 3 CI states to the higher terms using the ZINDO algorithm.[15,16,23] This particular step provides the inclusion of all the $a^4T_1$ components at any symmetry and contributes significantly to the completeness of the ESA spectrum. *(iii)* Lorenzian band simulation around each non-zero ESA peak and subsequent convolution of the delta functions to a normalized Lorenzian function of a proper width. The latter width has been set 1000 $cm^{-1}$, close to the average value observed in the ZnS:Mn absorption spectra.

The calculated ESA spectra are given in Figures 2a-d. These plots represent the JT $D_{2d}$ structures that can be obtained through distortions at different angles. The off-center $\tau_2$-mode produces ESA spectra that cannot be related with experiment (bands too high in energy), but its *e*-mode combination that leads to a structure of $C_{2v}$ symmetry gives ESA profiles similar to those in $D_{2d}$.

First we note that the ESA spectrum calculated for the $T_d$ geometry (Figure 2a) - transitions from the $a^4T_1$ state to higher lying terms - shows little resemblance to the experiment. An intense band is observed at about 15,000 $cm^{-1}$ (1.86 eV) that can be assigned to the experimental 1.9 eV band maximum, but there is a complete lack of other bands in the 1.1 - 2.3 eV region where the experimental spectrum was recorded.[9,10] This result strongly suggests that the excited state is not of $^4T_1$ type in $T_d$.

Further distortion of the tetrahedral environment around the $Mn^{2+}$ ion in the excited state, leads to the appearance of the experimental peaks as shown in Figures 2b-d. Examining the theoretical ESA structures and intensities, we can conclude that the best reproduction of the experimental ESA spectrum is obtained at relatively low values of the S-Mn-S angle distortions, corresponding to slight $D_{2d}$ type atom rearrangements. The best fit with the experimental ESA spectrum has been obtained at S-Mn-S angle of 115°, close to the predictions based on the excited state energies by both *ab initio*[8] and semiempirical studies.[12]

In all cases displayed in Figure 2, a group of IR bands centered at about 4000 $cm^{-1}$ (0.5 eV) is present in the ESA spectrum. Contrary to the 1-2 eV peaks which are dominated by Mn $3d$-configurations of the type $e^2$(triplet)$t_2^3$(doublet), these particular IR bands have their origin from states $e^1$(doublet)$t_2^4$(triplet) that involve $e \rightarrow t_2$ electron transitions. The existence of these bands needs experimental verification.

Finally we would like to mention, once again, that the present ESA simulation should be viewed as further evidence of the presence of a strong JT effect for the ZnS:Mn excited states. The theoretical ESA spectrum is calculated by the superposition of a large set of initially $T_d$ split terms that stem from a coupling with the JT active $e$-mode, and is therefore a characteristic of the whole assembly of excited states rather than the first excited state alone.

## ACKNOWLEDGMENT

This work was supported in part through a grant from the Office of Naval Research.

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Table 1 Term splittings for different symmetries involved in the JT distortions.

| $T_d$ | $D_{2d}$ | $C_{3v}$ | $C_{2v}$ |
|---|---|---|---|
| $T_1$ | $A_2$+E | $A_2$+E | $A_2$+$B_1$+$B_2$ |
| $T_2$ | $B_2$+E | $A_1$+E | $A_1$+$B_1$+$B_2$ |
| E | $A_1$+$B_1$ | E | $A_1$+$A_2$ |
| $A_1$ | $A_1$ | $A_1$ | $A_1$ |
| $A_2$ | $B_1$ | $A_2$ | $A_2$ |

Table 2  Calculated and experimental band energies (eV) for ZnS:Mn; *ab initio* data taken from Ref. 4.

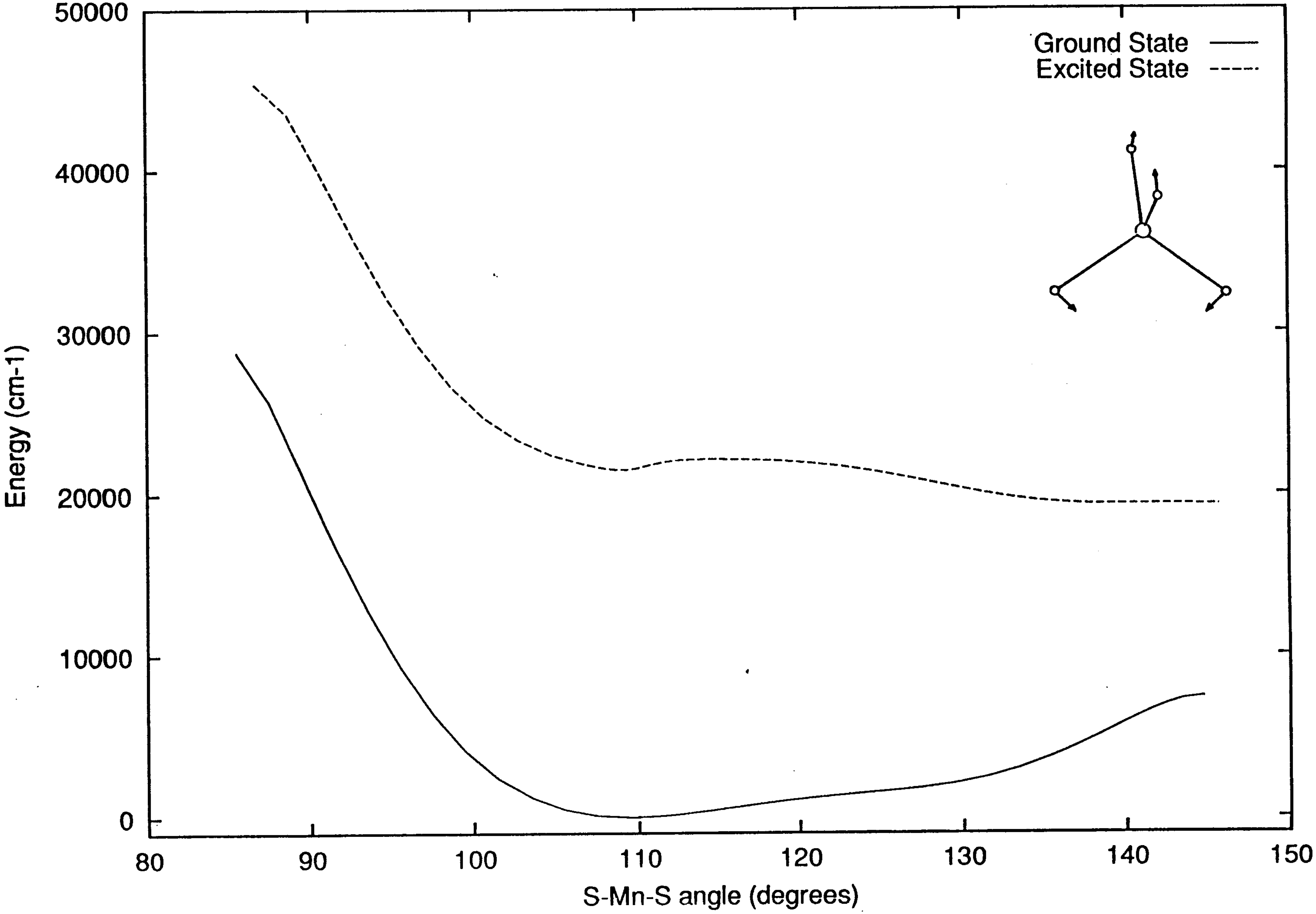
| Tansition | Ab initio | This work | Experiment |
|---|---|---|---|
| $^6A_1 \rightarrow a^4T_1$ | 2.68 | 2.72 | 2.34 |
| $\rightarrow a^4T_2$ | 2.83 | 2.76 | 2.49 |
| $\rightarrow a^4E$ | 2.96 | 2.78 | 2.67 |
| $\rightarrow\ ^4A_1$ | 2.96 | 2.78 | 2.67 |
| $\rightarrow b^4T_2$ | 3.31 | 3.18 | 2.89 |
| $\rightarrow b^4T_1$ | 3.39 | 3.47 | 3.19 |
| $\rightarrow b^4E$ | 3.52 | 3.56 | - |

## Figure Captions

Figure 1 (a) Ground and first excited state energies as a function of the e-mode distortion parameter, the ground state $^6A_1$ energy at $T_d$-geometry taken as a reference. (b) closer view of the local minima observed for the $a^4T_1$ state. (c) ground and first excited state potential curves produced by the $\tau_2$-mode.

Figure 2 Excited state absorption (ESA) spectra calculated for: (a) the initial $T_d$ structure, and the $D_{2d}$-geometries resulting from the e-mode distortion by (b) 5°, (c) 10° and (d) 15° of the initially tetrahedral S-Mn-S angles. Dashed lines indicate the positions of calculated ESA peaks.

Figure 1a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20000
10000
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120
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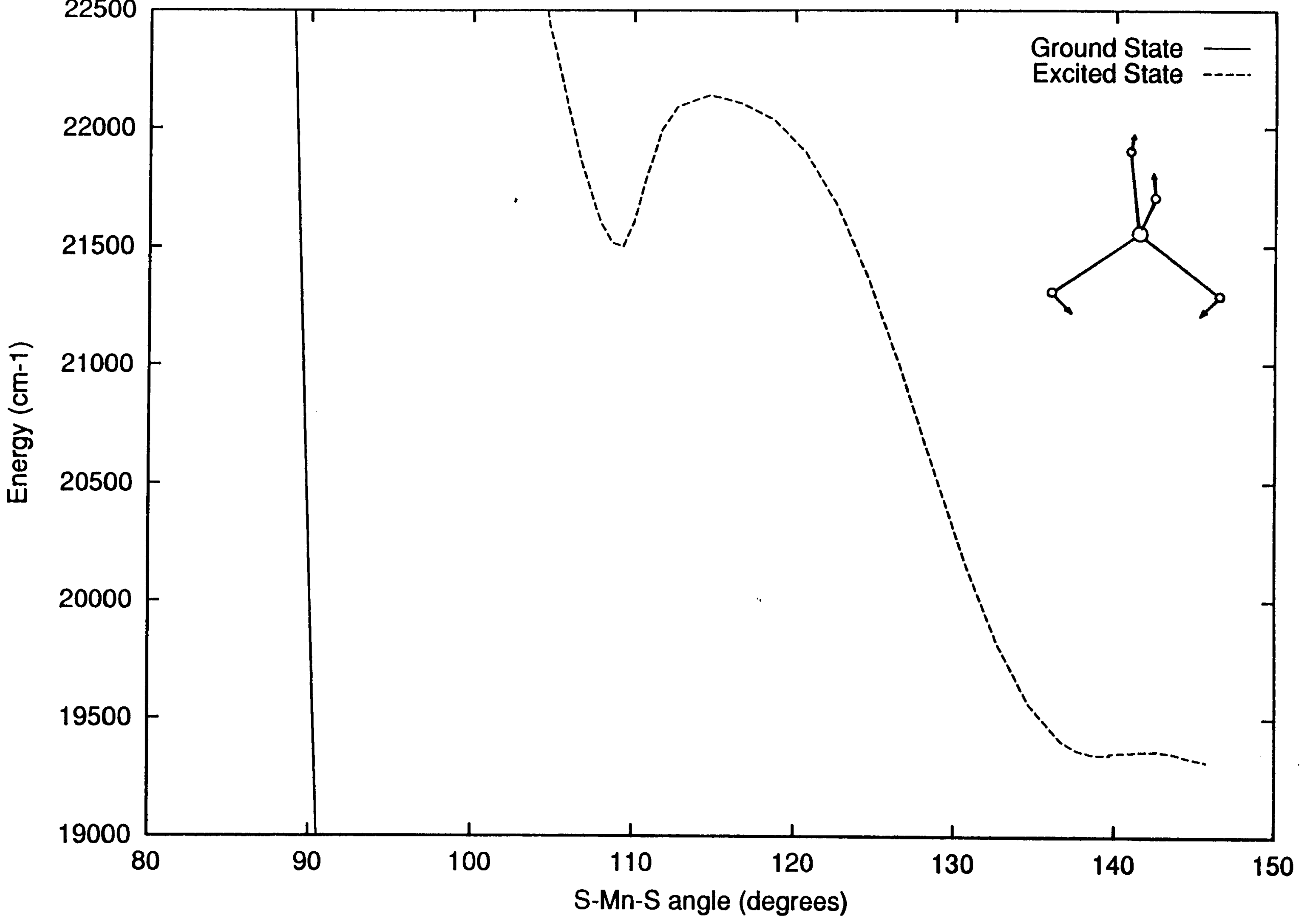
S-Mn-S angle (degrees)
Ground State
Excited State

Figure 1b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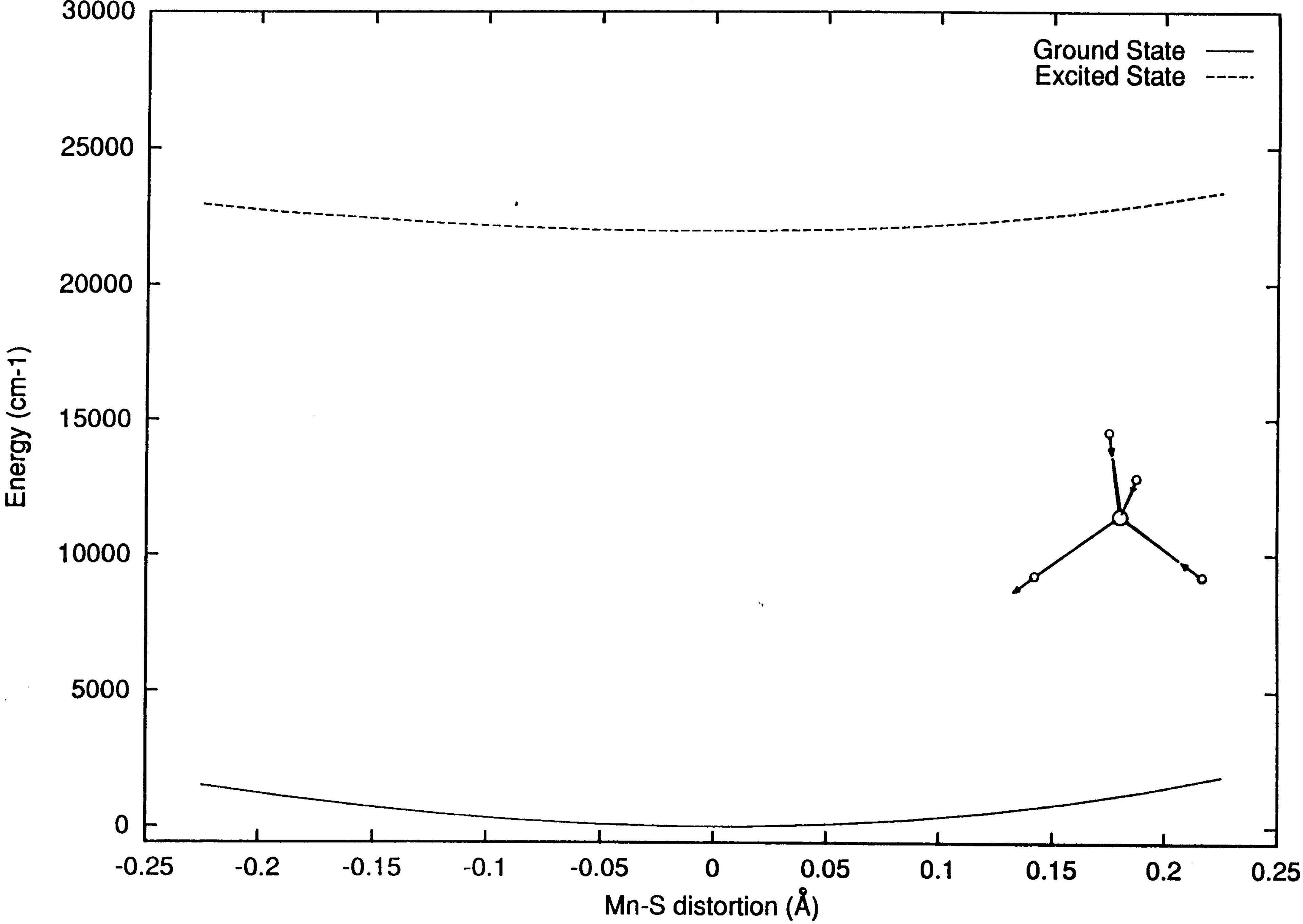
S-Mn-S angle (degrees)
Ground State
Excited State

Figure 1c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Excited State
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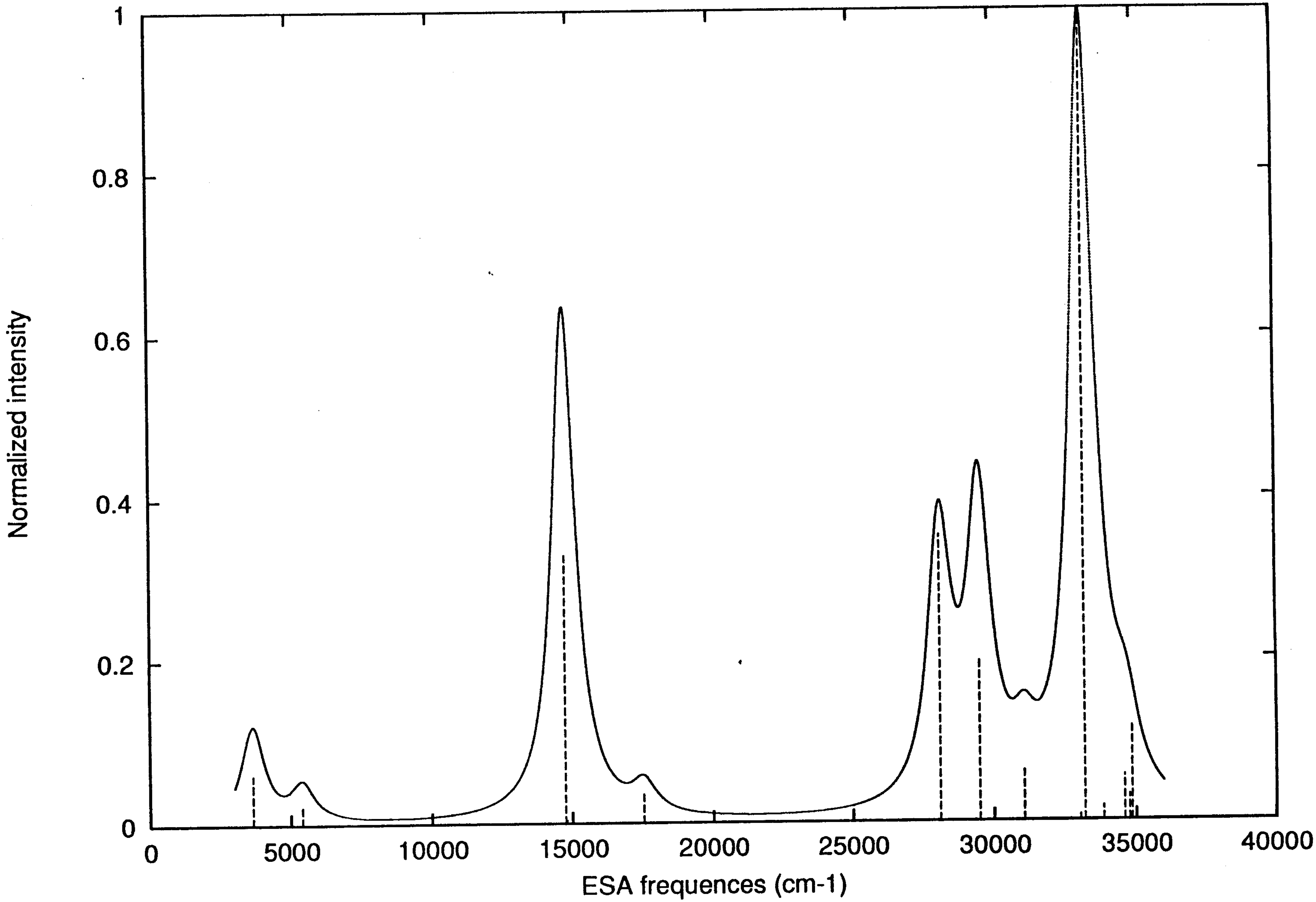
0.25
Mn-S distortion (Å)

Figure 2a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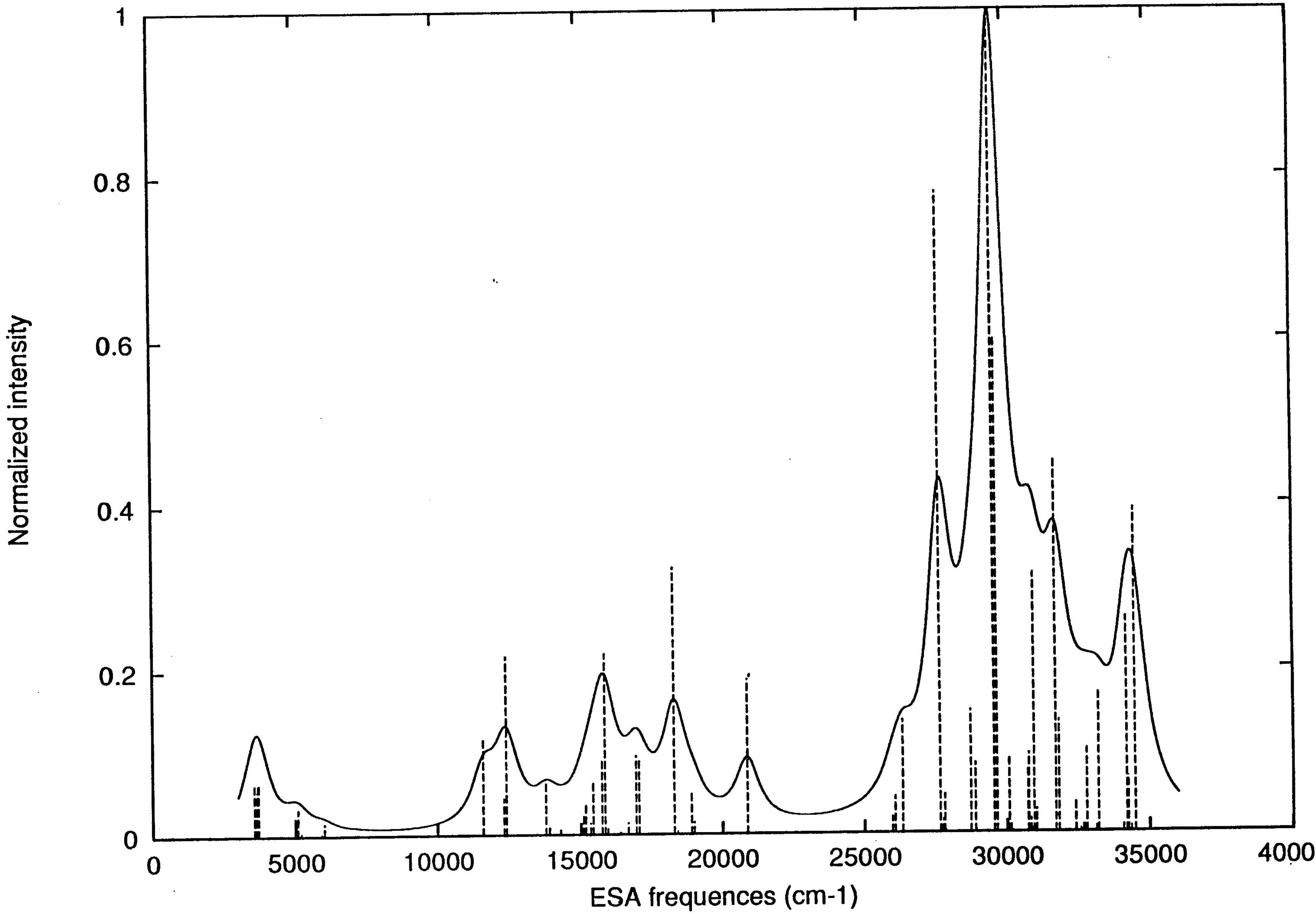
ESA frequences (cm-1)

Figure 2b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0.8
0.6
0.4
0.2
0
0
5000
10000
15000
20000
25000
30000
35000
40000
ESA frequences (cm-1)

Figure 2c

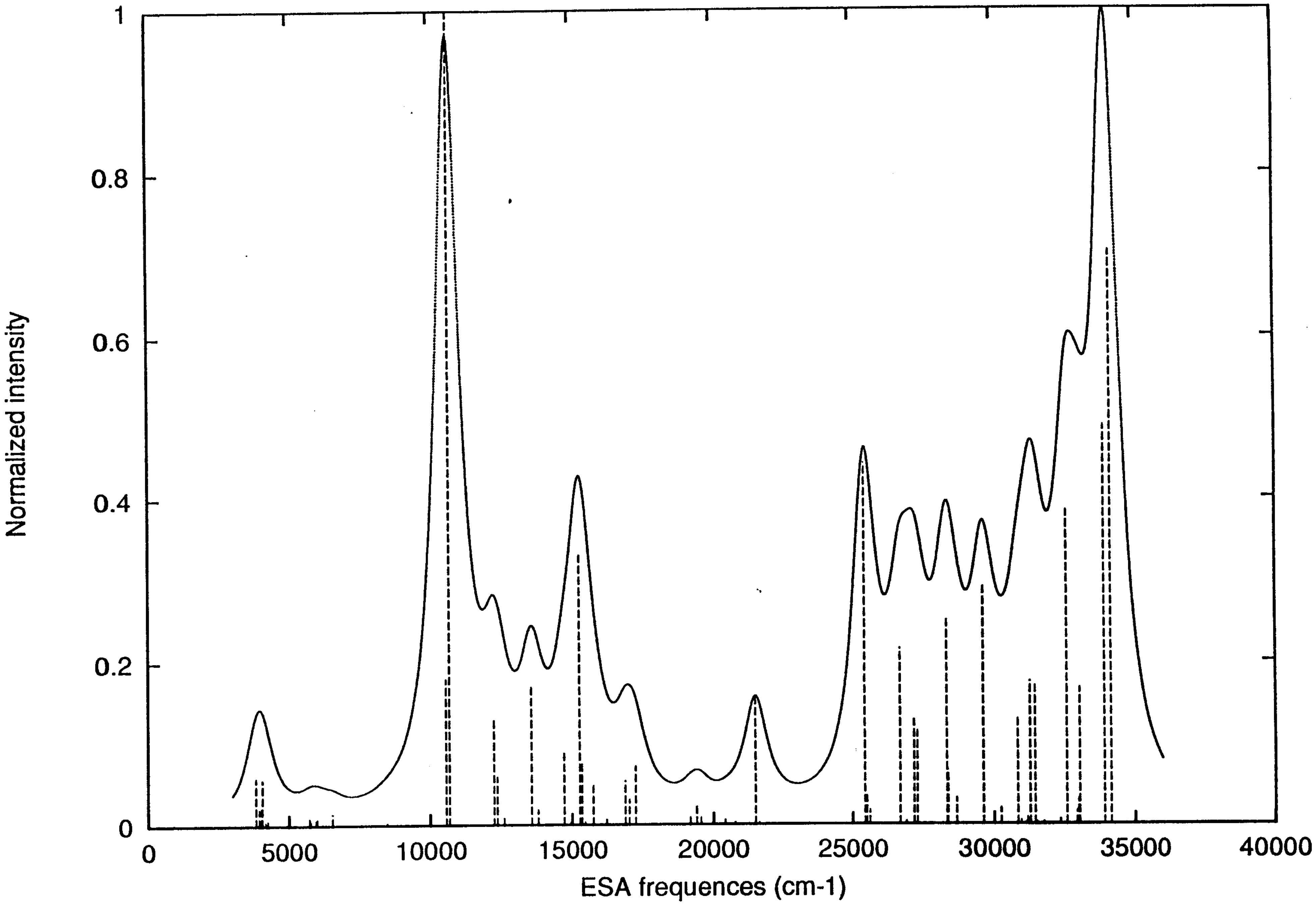
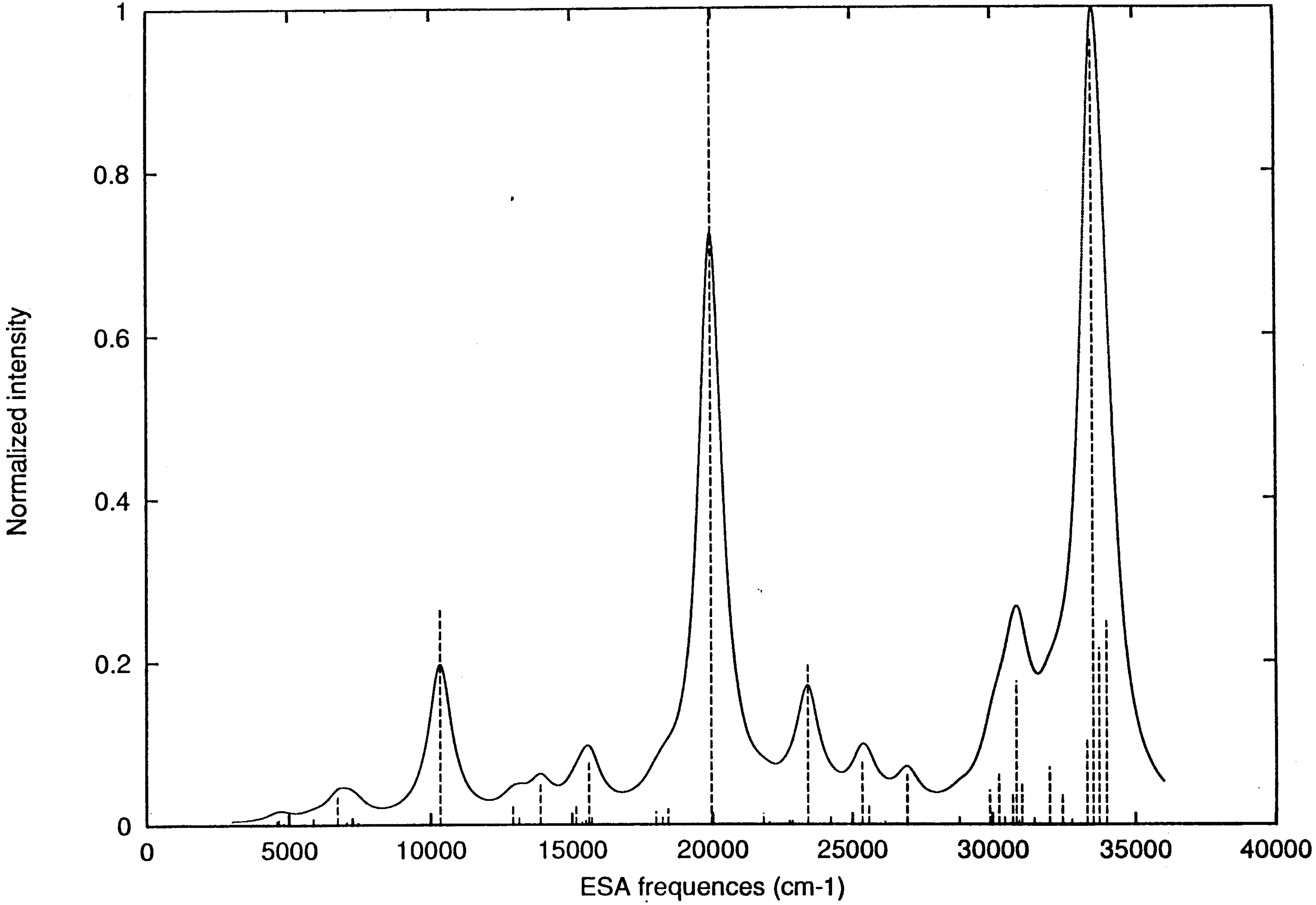

Normalized intensity
0
0.2
0.4
0.6
0.8
1
0
5000
10000
15000
20000
25000
30000
35000
40000
ESA frequences (cm-1)

Figure 2d


Normalized intensity
0
0.2
0.4
0.6
0.8
1
0
5000
10000
15000
20000
25000
30000
35000
40000
ESA frequences (cm-1)