Energy States in Solids With Particular Reference to NdCl36H2O

F. H. Spedding and H. F. Hamlin

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of vibrational origin are clearly present at 20° but rapidly vanish as the temperature is increased.

Not only do the lines vanish but the general absorption seems to vanish as well. This effect was present for Sm but is much more pronounced here. It would appear from this that as the crystal takes up vibratory motion a point is reached where sharp quantization of this vibratory motion suddenly disappears. For a proper study of this vibratory motion a number of plates should be taken at hydrogen tempera-

tures using crystals and conglomerates of various thicknesses so that the spectra of each region could be studied under the most favorable conditions, but, unfortunately, liquid hydrogen is not at present available at Cornell.

We wish to express our thanks to Dr. Nutting, Dr. Meehan and Mr. Kraus of the University of California for their kindness in photographing the Pr at hydrogen temperatures. We also wish to thank Professor R. C. Gibbs for allowing us to use the facilities of the Cornell physics department.

Energy States in Solids With Particular Reference to NdCl₃6H₂O

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The absorption spectra of $NdCl_3 6H_2O$ has been photographed at 78°K, 169°K and 200°K. Two low lying excited states were found, located at 62 and 250 cm⁻¹ above the basic state. These three levels presumably arise from a splitting of the basic state of $Nd^{+++}(^4J_{9/2})$ in a predominantly cubic field. The over-all splitting is slightly smaller than that which was found for the sulphate, and the relative splitting is slightly different. The differences reflect the change in crystal field which is brought about by the break in the homologous series of the hydrated chlorides of the rare earths between Nd and Pr.

THE atoms in a solid are so close together that they exert powerful electric fields on each other and thus cause the energy states of the atoms to split into a number of components. The nature of this splitting depends, of course, on the energy state involved and on the symmetry and position of the neighboring atoms in the solid. This problem has been treated theoretically by a number of investigators, notably Bethe[2] and Van Vleck.[3] Penney and Schlapp[4] have treated the specific case of $Nd_2(SO_4)_3 8H_2O$. They found that the variation of the experimental magnetic susceptibility with temperature could be accounted for very nicely if they assumed that the rare earth ions were surrounded by a cubic field, presumably brought about by

the octahedron of oxygen atoms which surround the rare earth ion. They predicted that the basic state would split into three levels with a **relative** separation of 0, 243 and 834 cm⁻¹. Mr. Hamlin, Dr. Nutting and I investigated the salt spectroscopically and found three levels at 0, 77 and 260 which have the same relative separation as the levels predicted.[5] Further, using our values in Penney and Schlapp's equations, excellent agreement was obtained with the magnetic susceptibility measurements of a number of investigators.[5, 6]

In deriving their equations Penney and Schlapp used a potential energy function of the form $V = (x^4 + y^4 + z^4)$. They neglected all other terms, and the experimental results justified their being neglected. If any rhombic terms had

[1] Baker Research Fellow.
[2] Bethe, Ann. d. Physik **3**, 133 (1929).
[3] J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Oxford, 1932). Phys. Rev. **41**, 208 (1932), etc.
[4] Penney and Schlapp, Phys. Rev. **41**, 194 (1932).
[5] Spedding, Hamlin and Nutting, J. Chem. Phys. **5**, 191 (1937).
[6] Spedding, Phys. Rev. **50**, 574 (1936); Spedding, J. Chem. Phys. **5**, 160 (1937).

been present, one would have expected a further splitting of some of the levels and none was observed. The calculated splitting pattern of course depends directly on the nature of the potential equation used in the calculation. This equation itself is directly determined by the position and symmetry of the surrounding atoms. Thus, if one determines the splitting experimentally, then, theoretically, one should be able to determine the form of this equation and, therefore, the position and distance of the envelope of atoms surrounding the rare earth ion being studied. If this can be done, a powerful tool will be available to study short range order in a solid or solution, and it will be of assistance in x-ray studies in a region where such information can be obtained only with difficulty. The establishment of this tool, however, awaits the existence of more experimental data upon which it can be tested and we are making a systematic attempt to obtain such data. This paper is one of a series in which we are presenting the material obtained.

$NdCl_36H_2O$ crystallizes in the monoclinic system.[7] The six oxygens of the water molecules are almost certainly grouped about the Nd ion in the form of an octahedron so that the predominating field will be cubic and as a first approximation the splitting of the lowest state of the chloride should be the same as the sulphate. In the analogous case of the chloride and sulphate of Gd the fields are so similar that their spectra are almost identical.[8] In Nd, however, some differences would be expected, for if one examines the homologous series of the hydrated chlorides of the rare earths, one finds that they are all $6H_2O$ except Pr, Ce and La, which are $7H_2O$. This means that as the size of the rare earth ion increases due to a smaller total charge on the nucleus, the lattice slowly expands until with Pr it has become large enough to permit an extra water molecule to enter the lattice. In Nd, which is the next element to Pr in the series,

the lattice evidently is not large enough to permit the extra water to be present, but there is extra space, which will permit the octahedron of water molecules to expand slightly into it. One would therefore predict that the over-all splitting of the lowest state of $NdCl_36H_2O$ would be somewhat smaller than the corresponding case of the $Nd_2(SO_4)_38H_2O$ (where the homologous series does not break down until La is reached). The distortion of the field which will take place when this occurs will, of course, have to be determined either from our experiments or from x-ray studies.

EXPERIMENTAL

The $NdCl_36H_2O$ was prepared from some fairly pure Nd supplied by Dr. H. N. McCoy. The chloride was prepared by dissolving the oxide in HCl and then slowly evaporating the solution at room temperatures until the salt crystallized out. This salt was recrystallized once from distilled water. Photographs were made of both a single crystal about $1\frac{1}{2}$ mm thick and of the conglomerate of small crystals 6 mm thick. The conglomerate has a tendency to bring out very faint lines, for, as has been pointed out elsewhere,[9] when light enters these small crystal fragments it is totally reflected a number of times before it emerges. As the refractive index of the salt increases very rapidly near an absorption band, the effective path length of light of that frequency would be very large. The strong absorption lines would appear about the same in both the single crystal and conglomerate, since the light in the center of the band would be completely absorbed in both cases. Increasing the path length of the light would therefore not have much effect on the plate except to broaden the line slightly. The very faint lines, however, would be much enhanced in the conglomerate over the single crystal, since the extra path length here would deepen the absorption as recorded by the plate.

All plates were photographed on a grating belonging to the physics department which had a dispersion of about 4.63A per mm. Plates were taken when the crystals were immersed directly in liquid nitrogen (78°K) and liquid ethylene

[7] Accurate crystallographic measurements have not been made for $NdCl_26H_2O$. However, they will not be very different from $SmCl_36H_2O_4$ which has axial ratios $a : b : c$ $= 14713 : 1 : 12182$ and angle $= 86° 34'$. See "The Crystallography of Some Rare Earth Halides," Adolf Pabst, Am. J. Science, 22, 426 (1931).

[8] Spedding and Nutting, J. Am. Chem. Soc. 55, 496 (1933).

[9] Spedding and Bear, Phys. Rev. 39, 948 (1932).

TABLE I.

Single	Nitrogen temperature 78°K				Ethylene 169°K		CO₂ acetone 200°K		Type
	Crystal	Int.	Conglom.	Int.	Conglom.	Int.	Conglom.	Int.	
6838.1' 6835.5 6838.1'	14,620.' 14,625. 14,631.'	5wd			14,625.	2d			h
6814.2	14,671.	0d							h
6806.5	14,688.	3s			14,687.	3d			l
6797.4	14,707.	1vd							h
6786.9' 6785.5 6784.1'	14,730.' 14,733. 14,736.'	6d			14,731.	6d			l
6768.8	14,770.	5d			14,767.	5d			l
6755.8' 6751.9 6748.1'	14,798.' 14,807. 14,815.'	7wvd			14,793.' 14,808. 14,822.'	6d			
6728.3' 6726.1 6723.7'	14,859.' 14,863. 14,869.'	6vd			14,850.' 14,866. 14,886.'	6d			
							15,663.' 15,678. 15,716.'	0vwd	h
			15,746.	0vd	15,737.' 15,746. 15,758.'	1d	15,735.' 15,747. 15,760.'	1wd	h
					15,766.' 15,773. 15,781.'	0d	15,768.'		h
			15,800.	1d	15,789.' 15,802. 15,816.'	1d		vwd	h
			15,813.	0d					h
			15,825.	2d	15,825.	0d	15,824.'		h
			15,842.	1d					
6303.6	15,860.	2d	15,858.' 15,861. 15,864.'	5d	15,863.	2d	15,853.' 15,860. 15,870.'	2wd	l, h
			15,875.	3d	15,877.	1s			l, h
6293.1	15,886.	4s	15,887.	10s	15,888.	3s	15,883.' 15,887. 15,892.'	2d	l
6279.7' 6278.9 6278.1'	15,920.' 15,922. 15,924.'	8s	15,916.' 15,922. 15,927.'	10d	15,918.' 15,923. 15,928.'	8d	15,916.' 15,924. 15,930.'	9d	l
6273.1	15,937.	5s	15,934.' 15,938. 15,941.'	10d	15,934.' 15,938. 15,941.'	7d	15,931.' 15,937. 15,942.'	7d	l
6264.3	15,959.	2d	15,956.' 15,959. 15,962.'	6d	15,961.	3d	15,954.' 15,960. 15,966.'	4d	h

TABLE I.—*Continued.*

SINGLE	NITROGEN TEMPERATURE 78°K				ETHYLENE 169°K		CO₂ ACETONE 200°K		TYPE
	Crystal	Int.	Conglom.	Int.	Conglom.	Int.	Conglom.	Int.	

⎰ 6254.5′
⎱ 6252.8
  6251.0′
	⎰ 15,984.′
	⎱ 15,989.
	  15,993.′
		3d	⎰ 15,984.′
			⎱ 15,991.
			  15,998.′
				7d	⎰ 15,984.′
					⎱ 15,991.
					  15,998.′
						4d	⎰ 15,980.′
							⎱ 15,991.
							  16,000.′
								5wd	l

⎰ 6241.7′
⎱ 6240.3
  6238.9′
	⎰ 16,017.′
	⎱ 16,021.
	  16,024.′
		6d	⎰ 16,013.′
			⎱ 16,021.
			  16,028.′
				9wd	⎰ 16,016.′
					⎱ 16,021.
					  16,025.′
						8d	⎰ 16,014.′
							⎱ 16,022.
							  16,028.′
								8d	l

⎰ 6229.7′
⎱ 6228.6
  6227.6′
	⎰ 16,048.′
	⎱ 16,051.
	  16,053.′
		4d	⎰ 16,046.′
			⎱ 16,051.
			  16,056.′
				8d	16,050.	5d	⎰ 16,042.′
							⎱ 16,050.
							  16,055.′
								5d	l

							⎰ 16,071.′ ⎱ 16,076. 16,082.′	2d	
			16,692.	0d					h
			16,705.	0d					h
5968.0	16,752.	2d	16,755.	4d					l
5962.3	16,768.	1vd	16,767.	3d					l
5822.9	16,879.	3vd	⎰ 16,877.′ ⎱ 16,885. 16,891.′	4d					h
5912.3	16,909.	3vd	⎰ 16,906.′ ⎱ 16,911. 16,918.′	5d					h
			⎰ 16,918.′ ⎱ 16,926. 16,936.′	3dw					
			⎰ 16,944.′ ⎱ 16,955. 16,969.′	1ws					
			16,979.	2d					
			17,021.	2d					
			⎰ 17,047.′ ⎱ 17,056. 17,064.′	3wd					
5856.7	17,070.	8s	⎰ 17,064.′ ⎱ 17,070. 17,076.′	8s					h

⎰ 5850.1
⎱ 5846.6
  5843.3
	⎰ 17,089.′
	⎱ 17,099.
	  17,109.′
		7wd	⎰ 17,080.′
			⎱ 17,099.
			  17,117.′
				6vwd					h

5835.9	17,131.	9s	⎰ 17,127.′ ⎱ 17,131. 17,136.′	9d					l
⎰ 5830.7′ ⎱ 5817.6′	⎰ 17,146.′ ⎱ 17,185.′	8vws	17,144.′						l
5813.8	17,196.	5s							

TABLE I.—*Continued.*

SINGLE	NITROGEN TEMPERATURE 78°K				ETHYLENE 169°K		CO₂ ACETONE 200°K		TYPE
	Crystal	Int.	Conglom.	Int.	Conglom.	Int.	Conglom.	Int.	
$\begin{cases} 5812.0' \\ 5786.6' \end{cases}$	$\begin{cases} 17,201.' \\ 17,276.' \end{cases}$	7vwd							
$\begin{cases} 5781.9' \\ 5775.9' \end{cases}$	$\begin{cases} 17,291.' \\ 17,309.' \end{cases}$	8ws							
$\begin{cases} 5771.6' \\ 5765.1' \end{cases}$	$\begin{cases} 17,321.' \\ 17,341.' \end{cases}$	8wd		6vwd					
5758.7	17,360.	8d							
$\begin{cases} 5747.8' \\ 5737.9' \end{cases}$	$\begin{cases} 17,393.' \\ 17,423.' \end{cases}$	7vwd							
$\begin{cases} 5734.1' \\ 5708.2' \end{cases}$	$\begin{cases} 17,435.' \\ 17,514.' \end{cases}$	7vwd	17,526.'						
			$\begin{cases} 17,539.' \\ 17,548. \\ 17,555.' \end{cases}$	5wd					
			$\begin{cases} 17,567.' \\ 17,573. \\ 17,580.' \end{cases}$	5wd					
			$\begin{cases} 17,615.' \\ 17,678.' \end{cases}$	4vwd					
			$\begin{cases} 17,694.' \\ 17,703. \\ 17,712.' \end{cases}$	2wd					
			18,652.	0d	$\begin{cases} 18,640.' \\ 18,655. \\ 18,666.' \end{cases}$	3vd			
			18,686.	0d	$\begin{cases} 18,680.' \\ 18,693. \\ 18,707.' \end{cases}$	2vd			
			18,752.	2d	$\begin{cases} 18,745.' \\ 18,753. \\ 18,763.' \end{cases}$	3vd			h
			18,786.	3d	$\begin{cases} 18,778.' \\ 18,789. \\ 18,804.' \end{cases}$	3vd			
			18,818.	1d					
			18,847.	2d	$\begin{cases} 18,842.' \\ 18,850. \\ 18,860.' \end{cases}$	2vd			
			18,865.	0d					
			18,898.	0wd	$\begin{cases} 18,882.' \\ 18,893. \\ 18,903.' \end{cases}$	2vd			
			$\begin{cases} 18,920.' \\ 18,925. \\ 18,933.' \end{cases}$	3d					
$\begin{cases} 5279.8' \\ 5278.1 \\ 5376.8' \end{cases}$	$\begin{cases} 18,935.' \\ 18,941. \\ 18,946.' \end{cases}$	8d	$\begin{cases} 18,940.' \\ 18,945.' \end{cases}$	8d	$\begin{cases} 18,920.' \\ 18,934. \\ 18,953.' \end{cases}$	3vd			h

TABLE I.—*Continued.*

SINGLE	NITROGEN TEMPERATURE 78°K				ETHYLENE 169°K		CO₂ ACETONE 200°K		TYPE
	Crystal	Int.	Conglom.	Int.	Conglom.	Int.	Conglom.	Int.	
5271.0′ 5270.3 5269.2′ 5268.3 5267.6′	18,966.′ 18,969. 18,973.′ 18,976. 18,979.′	10s 10s	18,967. 18,976.	8s 8s	18,965.′ 18,976. 18,985.′	3vd			
5261.2	19,002.	10vs	19,001.	10s	18,999.	3d			l
5254.6′ 5253.1 5251.7′ 5250.3 5248.9′	19,026.′ 19,031. 19,037.′ 19,041. 19,046.′	9d 9d	19,014.′ 19,056.′	8vwd	19,015.′ 19,056.′	3vd			
5240.0′ 5238.6 5237.4′	19,079.′ 19,084. 19,088.′	7d	19,071.′ 19,078. 19,085.′	7d					
					19,072.′ 19,088. 19,109.′	3vd			
5236.3′ 5234.9 5233.3′	19,092.′ 19,097. 19,103.′	9d	19,087.′ 19,096. 19,105.′	8wd					
			19,115.	5d					
5227.3′ 5225.9 5224.6′ 5223.7 5222.3′	19,125.′ 19,130. 19,135.′ 19,138. 19,142.′	4vd 10vd	19,121.′ 	8vwd	19,123.′	3vd			
5221.2′ 5219.9 5218.8′ 5216.3 5213.7′	19,147.′ 19,152. 19,156.′ 19,165. 19,175.′	10vd 4vd	19,177.′		19,183.′				
5207.3′ 5204.5 5201.4′	19,198.′ 19,209. 19,220.′	3wd	19,194.′ 19,209. 19,221.′	6wd	19,193.′ 19,210. 19,226.′	2vd			
			19,311.	2d	19,266.′	3vd			
5164.5	19,357.	3d	19,358.	6d	19,375.′				
			19,400.	1d					h
			19,417.	3d					h
5139.3	19,452.	3d	19,451.	6d	19,441.′				
5136.0	19,465.	4d	19,463.	7d					l
5132.1	19,479.	4d	19,479.	6d					l
5126.0′ 5122.0 5118.6′	19,503.′ 19,518. 19,531.′	10wd	19,495.′	6vwd		3vd			
5117.1′ 5115.8 5114.3′	19,537.′ 19,542. 19,548.′	10s	19,550.′						
5106.7′ 5104.5 5102.0′	19,576.′ 19,585. 19,594.′	9wd	19,572.′ 19,586. 19,601.′	5vwd					

TABLE I.—*Continued.*

	NITROGEN TEMPERATURE 78°K				ETHYLENE 169°K		CO₂ ACETONE 200°K		
SINGLE	Crystal	Int.	Conglom.	Int.	Conglom.	Int.	Conglom.	Int.	TYPE
5094.9' 5092.3 5089.6' 5087.3 5084.9'	19,622.' 19,632. 19,642.' 19,651. 19,660.'	7wvd 2wvd	19,625.' 19,659.'	5vwd	19,613.' 19,623.'	3vd			
5082.1	19,671.	1vd	19,671.	4d					
			19,733.	2d	19,696.'				
					19,793.'				
5039.2' 5036.5 5034.0'	19,839.' 19,849. 19,860.'	6wd	19,835.' 19,846. 19,857.'	5wd					
5023.5' 5021.0 5018.6'	19,900.' 19,911. 19,920.'	8wd	19,886.' 19,908. 19,927.'	6vwd		3vd			
5007.8	19,963.	2vd	19,949.' 19,969. 19,990.'	4vwd	20,001.'				
			20,053.	2vd					
			20,199.	1vd					
			20,211.	0vd					
			20,324.	2vd					
			20,390.	3d					
			20,414.' 20,427. 20,437.'	4wd	20,414.' 20,427. 20,441.'	2vd			
			20,451.' 20,457. 20,466.'	4d	20,453.'				
			20,473.' 20,480. 20,484.'	5d		3vd			
			20,491.' 20,498. 20,505.'	5wd	20,506.'				
			20,516.' 20,523. 20,531.'	5wd					
			20,543.' 20,558. 20,573.'	5vwd	20,545.' 20,558. 20,571.'	3vd			
			20,588.' 20,597. 20,606.'	5wd	20,583.' 20,611.	1vd			
			20,616.' 20,625. 20,635.'	5wd	20,634.'				h

TABLE I.—*Continued.*

| | NITROGEN TEMPERATURE 78°K | | | | ETHYLENE 169°K | | CO₂ ACETONE 200°K | | |
SINGLE	Crystal	Int.	Conglom.	Int.	Conglom.	Int.	Conglom.	Int.	TYPE
4838.8	20,661.	9vs	20,660.	8s	20,664.	7d			
			20,672.	8s	20,677.	7d			
			{ 20,684.' 20,695. 20,705.'	3wd					
			{ 20,721.' 20,727. 20,734.'	3d					
					{ 20,755.' 20,764. 20,771.'	4vd			h
{ 4808.5' 4805.9 4802.5'	{ 20,791.' 20,802. 20,817.'	1wd	{ 20,781.' 20,802. 20,820.'	5vwd	{ 20,782.' 20,799. 20,813.'	6vd	20,780.'		h
{ 4799.6' 4797.4 4795.3'	{ 20,830.' 20,839. 20,848.'	1wd	{ 20,827.' 20,837. 20,848.'	5wd	{ 20,833.' 20,856.	9vd			h
{ 4792.2' 4791.1 4789.5'	{ 20,862.' 20,866. 20,874.'	1d	{ 20,856.' 20,870. 20,887.'	5wd	20,883.'				l
			20,908.	1vd					
{ 4773.0' 4772.2 4771.4'	{ 20,945.' 20,949. 20,953.'	9d	{ 20,928.' 20,949. 20,963.'	7vwd	20,930.'			2vwd	h
						8vd			
{ 4766.9' 4766.0 4765.1'	{ 20,972.' 20,976. 20,981.'	8s	{ 20,969.' 20,976. 20,984.'	7wd	20,991.'				h
4758.3	21,010.	8vs	21,009.	8s	21,014.	8s			l
4757.0	21,016.	9vs	21,017.	8s					h
4752.0	21,038.	5s	{ 21,032.' 21,038. 21,043.'	8s	21,040.	8s	21,033.' 21,034.	·4d	l
4743.0	21,078.	9s	{ 21,070.' 21,080. 21,096.'	7wd	{ 21,070.' 21,079. 21,090.'	7vd	{ 21,064.' 21,080. 21,094.'	4vwd	l
{ 4732.8' 4731.3 4730.0'	{ 21,124.' 21,130. 21,136.'	7d	{ 21,109.' 21,128. 21,143.'	7vwd	{ 21,115.' 21,132. 21,151.'	7vd	{ 21,112.' 21,129. 21,153.'	4vwd	
4717.3	21,193.	5d	{ 21,183.' 21,189.	7vwd	{ 21,189.' 21,201. 21,211.'	6vd	{ 21,178.' 21,194. 21,208.'	4vwd	
4715.7	21,200.	9s	{ 21,204. 21,210.'	7vwd					
4708.9	21,231.	2d	{ 21,232.'	7vwd	{ 21,238.'		{ 21,235.'		
{ 4698.9' 4697.3 4695.6'	{ 21,276.' 21,283. 21,291.'	9wd	{ 21,284.'		21,264. 21,290.'	8vd	21,255. 21,278.'	4vwd	
			21,299.	2d					

TABLE I.—*Continued.*

SINGLE	NITROGEN TEMPERATURE 78°K				ETHYLENE 169°K		CO₂ ACETONE 200°K		TYPE
	Crystal	Int.	Conglom.	Int.	Conglom.	Int.	Conglom.	Int.	
4689.3	21,319.	2d	21,322.	3d	21,322.	1d	21,315.	4d	
4682.1′ 4681.2 4680.2′	21,352.′ 21,357. 21,361.′	7d	21,346.′ 21,356. 21,368.′	7wd	21,349.′ 21,358. 21,367.′	8d	21,358.	4d	
4674.3	21,388.	3d	21,392.	5d	21,392.	4d			
4666.7	21,423.	2d	21,425.	4d	21,425.	3d			
4660.2	21,453.	6s	21,445.′ 21,453. 21,462.′	6wd	21,453.	6d			
4653.1	21,485.	2d	21,477.′		21,481.′		21,456.′		
4647.4	21,512.	2d							
4641.1′ 4638.4 4636.1′	21.541.′ 21,553. 21,564.′	7wd			21,555.	9d			
4632.5	21,581.	1d		vwd				8vwd	
4629.0	21,597.	1d							
4617.3	21,652.	2wd							
					21,674.	9vd			
4608.5	21,693.	2d	21,733.′		21,733.′		21,717.′		
			21,773.	4d	21,779.	1d			
4569.8′ 4567.8 4565.8′	21,877.′ 21,886. 21,896.′	8wd	21,821.′ 22,000.′	7vwd	21,850.′ 21,900. 21,952.′	8vd	21,830.′ 22,003.′	8vwd	
				3vwd	22,035.′ 22,066. 22,102.′	1vd			
			22,092.′						
			22,153.	1vd					
			22,258.	1vd					
			22,290.′ 22,301. 22,310.′	3wvd					h
4474.3′ 4473.4 4472.4′	22,343.′ 22,348. 22,353.′	6d	22,335.′ 22,358. 22,381.′	8vwd	22,338.′ 22,366. 22,391.′	8vd	22,335.′ 22,364. 22,388.′	7vwd	l
4470.2′ 4469.1 4468.0′	22,364.′ 22,369. 22,375.′	6d	22,408. 22,418.	2vd 2vd					
4448.5	22,473.	4d	22,429.′ 22,475. 22,487.′	6vwd	22,462.′ 22,478. 22,491.′	4vd	22,455.′ 22,479. 22,494.′	3vwd	
4439.8	22,517.	2d	22,503.′ 22,517. 22,528.′	4wd	22,509.′ 22,528. 22,546.′	2vd	22,511.′ 22,532. 22,557.′	3vwd	
					22,975.	1d	22,976.	1d	h

TABLE I.—*Continued.*

| | NITROGEN TEMPERATURE 78°K | | | | ETHYLENE 169°K | | CO₂ ACETONE 200K° | | |
SINGLE	Crystal	Int.	Conglom.	Int.	Conglom.	Int.	Conglom.	Int.	TYPE
4339.8	23,036.	2d	$\begin{cases} 23,032.' \\ 23,039. \\ 23,045.' \end{cases}$	4d	$\begin{cases} 23,027.' \\ 23,040. \\ 23,053.' \end{cases}$	8d	$\begin{cases} 23,015.' \\ \\ 23,052.' \end{cases}$	9vwd	l, h
4332.4	23,075.	2d	$\begin{cases} 23,067.' \\ 23,081. \\ 23,092.' \end{cases}$	4wd	$\begin{cases} 23,064.' \\ 23,079. \\ 23,092.' \end{cases}$	8d	23,063.'		h
			23,099.	3s	23,100.	6d		8vwd	h
					$\begin{cases} 23,112.' \\ 23,124. \\ 23,137.' \end{cases}$	2d	23,111.'		
			23,159.	2d	$\begin{cases} 23,143.' \\ 23,154. \\ 23,164.' \end{cases}$	3d	23,154.	0vd	
			23,185.	1d	$\begin{cases} 23,170.' \\ 23,184. \\ 23,193.' \end{cases}$	2d			
4304.8	23,223.	7s	$\begin{cases} 23,216.' \\ 23,224. \\ 23,231.' \end{cases}$	9ws	$\begin{cases} 23,214.' \\ 23,226. \\ 23,237.' \end{cases}$	10d	$\begin{cases} 23,205.' \\ 23,224. \\ 23,243.' \end{cases}$	9vwd	h, l
					$\begin{cases} 23,214.' \\ 23,226. \\ 23,237.' \end{cases}$	10d			
4293.5	23,285.	10s	$\begin{cases} 23,269.' \\ 23,286. \\ 23,307.' \\ 23,324. \\ 23,339.' \end{cases}$	8wvs 2wd	$\begin{cases} 23,266.' \\ 23,287. \\ 23,307.' \\ 23,323. \\ 23,339.' \end{cases}$	10d 2d	$\begin{cases} 23,260.' \\ 23,287. \\ 23,313.' \end{cases}$	10vwd	l l
			23,351.	2s	23,347.	2d			l
			23,363.	3s	23,359.	2d			
4274.3	23,389.	3vd	$\begin{cases} 23,373.' \\ 23,389. \\ 23,402.' \end{cases}$	7vwd	$\begin{cases} 23,380.' \\ 23,390. \\ 23,402.' \end{cases}$	6d	23,397.	10d	
			$\begin{cases} 23,410.' \\ 23,412. \\ 23,415.' \end{cases}$	2d					
			23,435.	3d	$\begin{cases} 23,422.' \\ 23,430. \\ 23,438.' \end{cases}$	1s			
			23,452.	2d	23,452.	0d			
			23,471.	3s					
			23,482.	3d	$\begin{cases} 23,462.' \\ 23,481. \\ 23,494.' \end{cases}$	1s			
			23,497.	3d					
			$\begin{cases} 23,505.' \\ 23,522. \\ 23,543.' \end{cases}$	2vwd	$\begin{cases} 23,505.' \\ 23,523. \\ 23,538.' \end{cases}$	0s			
			$\begin{cases} 23,550.' \\ 23,559. \\ 23,573.' \end{cases}$	2wd					

TABLE I.—*Continued.*

Single	Nitrogen temperature 78°K				Ethylene 169°K		CO₂ acetone 200°K		Type
	Crystal	Int.	Conglom.	Int.	Conglom.	Int.	Conglom.	Int.	
4238.8	23,585.	1vd	23,584.' 23,597. 23,607.'	4wd	23,591.	2vd	23,586.	1d	
			23,612.' 23,622. 23,630.'	2wd					
			23,639.' 23,658. 23,675.'	2vwd					
4218.6	23,698.	4s	23,694.' 23,699. 23,703.'	5s	23,697.	4d	23,697.	1d	h
4207.8	23,759.	9vs	23,747.' 23,759. 23,770.'	8wd	23,747.' 23,759. 23,771.'	10vd	23,750.' 23,759. 23,770.'	4wd	l
4201.8	23,792.	3vd	23,787.' 23,801. 23,814.'	4dw	23,786.' 23,801. 23,816.'	4vd	23,789.' 23,800. 23,812.'	2wd	h
4190.5	23,857.	3vd	23,848.' 23,862. 23,875.'	4dw	23,859.	3vd	23,838.' 23,857. 23,862.'	1wd	l
4180.3	23,915.	5d	23,902.' 23,912. 23,922.'	6dw	23,902.' 23,913. 23,922.'	8d	23,902.' 23,914. 23,922.'	5wd	
			23,930.	3d		2d			
			23,950.	3d	23,953.'		23,949.	0d	
4159.1	24,037.	1d	24,042.	4s	24,039.	1d			
4153.2	24,071.	3s	24,074.	6s	24,072.	7d	24,069.	3d	
			24,378.	0d					
			24,408.	0d					
4073.5	24,542.	3s	24,543.	6s	24,544.	7s	24,544.	3d	
			24,617.	2s					
			24,635.	1d					
			24,651.	1d					
			24,698.	0d	24,699.	1vd	24,698.	1d	
			24,757.	0d	24,756.	1vd	24,750.	1d	
4025.4	24,835.	8s	24,837.	8s	24,831.' 24,838. 24,844.'	10s	24,830.' 24,837. 24,844.'	7d	
4013.7	24,908.	7s	24,908.	8s	24,907.	10d	24,900.' 24,913. 24,924.'	6wd	
4012.1	24,917.	7s	24,918.	8s	24,916.	10d			
			24,927.	3s					

TABLE I.—*Continued.*

	NITROGEN TEMPERATURE 78°K				ETHYLE? E 169°K		CO₂ ACETONE 200°K		
SINGLE	Crystal	Int.	Conglom.	Int.	Conglom.	Int.	Conglom.	Int.	TYPE
			24,947.	4s	24,945.	0d			
3830.3	26,100.	3s	26,105.	5s			26,099.	3d	
3821.4	26,162.	10s	26,163.	5s			26,159.	3d	
			26,250.	5s					

′ =band edge, d =diffuse, vd =very diffuse, w =wide about 15 cm⁻¹, s =sharp edges, h =line originating from low excited level, l =line originating from basic state.

(169°K) also at 200°K. A detailed description of the apparatus used in the photographing has been given elsewhere.[10]

The wave-lengths of the lines observed with their corresponding intensities are given in Table I. The intensities are based on an arbitrary scale of 0–10 and are of value only with regard to relative intensities of adjacent lines. Those marked 0 were so faint that they could not be seen under the comparator and had to be scratched with a needle under an eyeglass. Those marked with intensity 1 could be faintly seen under the comparator but were also scratched in order to locate them. All lines with intensity greater than 5 probably show complete absorption in the centers. Numbers above 5 merely indicate that the absorption is probably greater for the higher numbers, as the wings of the lines are better developed. It cannot be emphasized too strongly that the intensities given are only good for relative intensities of lines in the same region of the plate. Thus, in the regions of the plate where the background is weak due to lack of sensitivity of the plate, general absorption of the glass apparatus or to other causes, a line in which complete absorption takes place may be barely visible and therefore marked 2 or 3. The accuracy of measurement of the lines varies a great deal with the sharpness of the line, the region of the plate, etc. A general idea of the accuracy of measurement of each line can be obtained from Table I. In general, however, the frequencies can be depended upon to about 2 cm⁻¹. The absorption lines seem to originate from at least three lower states located at 0, 62 and 250 cm⁻¹. These lower levels were located

by two entirely independent methods. The first took advantage of the fact that the intensity of absorption line is proportional to the number of atoms in the lower state. These in turn are proportional to the temperature according to the Boltzman relationship. Therefore, the lines originating from a low lying excited state will suddenly fade out at some critical point as the temperature is lowered. From the temperature at which the lines fade out one can calculate roughly the separation of the levels. The second method takes advantage of the fact that if lines originating from the lower levels terminate in common upper levels the interval separations of the lower states will be repeated throughout the spectra. Tables II and III present some of the most striking cases of this constant interval repetition. The existence of the upper level was

TABLE II. *Neodymium chloride −62 cm⁻¹ levels. (Nitrogen conglomerate unless otherwise noted.)*

14,625 (xl)	−14,688 (xl)	63	
14,671 (xl)	−14,733 (xl)	61	
14,707 (xl)	−14,770 (xl)	63	
15,800	−15,861	61	?
15,813	−15,875	62	?
15,825	−15,887	62	
15,861	−15,922	61	
15,875	−15,937	62	
15,959	−16,021	62	
16,692	−16,755	63	
16,705	−16,767	62	
17,070	−17,131	61	
17,099	−17,161	62	
18,940	−19,001	61	
19,400	−19,463	63	
19,417	−19,479	62	
20,949	−21,009	60	
20,976	−21,038	62	
21,017	−21,080	63	
23,224	−23,286	62	
23,699	−23,759	60	
23,801	−23,862	61	

[10] Spedding and Bear, Phys. Rev. **42**, 58 (1932).

xl =single crystal.

absolutely certain as it is plainly evident by method 1. But it should be pointed out that the constant interval separation for these high levels is very difficult to locate, for as a rule at the temperature at which the lines from the excited state become intense all of the lines have become diffuse due to temperature broadening. The constant interval separation is made even more difficult to determine by the fact that the excited states in the multiplet occur close together and when the lines are broad the lines in the multiplets tend to fuse together. Nevertheless, we feel fairly confident that the upper state is located at 250 cm^{-1}.

DISCUSSION OF RESULTS

Second-order terms in the potential equation would be manifested by a further splitting of the 62 cm^{-1} and the 250 cm^{-1} levels. We were unable to detect any such splitting and unless unusual selection rules which would forbid all transitions to any upper state were operative, no splitting greater than 2 or 3 cm^{-1} occurred. Such selection rules seem unlikely and we concluded, therefore, that any second-order terms which might exist in the potential equation must be small. The rhombic splitting could not be greater than 1 or 2 percent of the cubic splitting. The over-all splitting of the basic state as might be expected was less than that for

TABLE III. *Neodymium chloride* -250 *cm*$^{-1}$ *levels.* (*169 degrees unless otherwise noted.*)

15,663′ (200 degrees)		
15,678	−15,924	
15,716′	−15,937	
15,746	−15,991	245
15,773	−16,021	248
15,802	−16,050	248
16,885 (nit)	−17,131 (nit)	246
16,911 (nit)	−17,161 (nit)	250
18,753	−18,999	246
20,625 (nit)	−20,870 (nit)	245
20,764	−21,009 (nit)	245
20,782′		
20,799	−21,040	
20,813′		
20,833′		
20,856	−21,079	
20,883′		
22,975	−23,226	251
23,040	−23,287	247
23,079	−23,323	244
23,100	−23,347	247

nit = 78°K.

the sulphate. The octahedron of oxygens presumably had expanded into the hole in the lattice and the fields about the Nd were thereby weaker. The relative separation of the lower levels was slightly different from that calculated by theory and found for the sulphate. The higher order terms in the potential equation, which it was found possible to neglect in the sulphate, were evidently more important here due to the distortion.

The excited multiplets experimentally can be divided into two groups. The first, as exemplified by the 14,700 and 15,800 cm^{-1} multiplets, consists of a few intense lines by themselves. The second group exemplified by the 17,000, 18,000 and 19,000 cm^{-1} multiplets consists of a number of intense lines associated with a large number of fainter ones. These fainter lines are so close together that with thick conglomerates they tend to fuse together to give a continuum. They resemble the band lines which one observes in polyatomic molecules and presumably are due to superimposed vibrational frequencies. Even with thick conglomerates no evidence of these associated lines has been found for the red multiplets. On the other hand, in the violet, certain multiplets which resemble the first type do show faintly some associated lines when very thick conglomerates are used. Whether or not these associated lines appear is not a matter of relative intensities, for the 14,600 multiplet is one of the most intense in the spectra, since it can be detected when only minute quantities of Nd salt are present and when most of the other multiplets are completely invisible.

An excited state can arise in either of two ways. First it can be a "forbidden" transition of the type $4f^3 - 4f^3$. Van Vleck[11] has discussed this type of transition in detail and believes that the observed transitions are all of this type. With the present state of theory a number of difficulties arise if one takes this position. For example, the number and position of the excited states are not in good agreement with it. Since the basic and excited states both arise from the same electronic configuration, the potential field equation for both states should be the same and as the number of excited states is limited by

[11] J. H. Van Vleck, J. Phys. Chem., Jan. (1937).

Pauli's principle one can calculate the splitting patterns for these various states. In the sulphate the agreement with excited states was not good even though it was excellent for the lowest state. There were always too many lines in the multiplet, and usually the intervals and over-all separations were wrong. In a few cases, e.g., in the 14,600 multiplet the splitting pattern of five of the six lines could be considered in very fair agreement with some of the possible states ($^2K_{15/2}$ or $^2L_{15/2 \text{ or } 17/2}$) but the sixth line which had to be neglected was one of the most intense in the group and differed in no way from the others. Also, the matrix coefficients q were very different from that required.

The second possibility is that the transition would be of the type $4f^3 - 4f^25x$. This supposition is attractive for the second type of multiplet as one would expect the vibrational frequencies to couple with the electron frequency more readily if one of the electrons were outside the completed $5s\ 5p$ shells. This idea is further borne out by the fact that so far we have not found any vibrational states associated with the lower states and that these associated lines are most pronounced in Pr where only two electrons give rise to the multiplets. On the other hand this supposition as pointed out by Van Vleck[11] is open to serious objections such as wrong order of intensity of lines, etc.

We shall discuss the problem of the excited states in much more detail in a later paper as we feel that the problem requires more experimental data before it can be discussed profitably. We have photographed a number of salts in which the potential fields are slightly different and by studying how the excited levels vary from salt to salt we hope to be able to learn a good deal more about the nature of these states.

We wish to thank Dr. H. N. McCoy for his generous gift of the Nd salt used in these investigations and Professor Gibbs of the physics department for extending to us the facilities of his department.

The Normal Vibrations and the Vibrational Spectrum of C_2H_6*

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An investigation is made of the vibrations, frequencies and selection rules of C_2H_6, which is assumed to have an internal rotational degree of freedom subject to a restricting potential of an arbitrary magnitude. Making use of the fact that the total potential energy of such a molecule is invariant under a reflection in a plane perpendicular to the threefold symmetry axis, a set of vibrational selection rules is obtained which is more complete than that of Teller and Topley who made use only of the invariance of the potential energy under operations of the point group D_3. The vibrational selection rules are found to be essentially the same for all degrees of restriction of the internal rotation except for the rules governing the appearance of the degenerate frequencies in the Raman spectrum, so that even in the limit of free rotation only one type of degenerate vibrational frequency is active in the infrared spectrum. A normal coordinate treatment based on a three-constant potential function of the valence force type is found to give a set of frequencies in good agreement on the whole with the observed frequencies. The fundamental region of the vibrational spectrum seems to afford no conclusive evidence for or against free internal rotation.

I N the present paper a theoretical study is made of the vibration spectrum of C_2H_6 in which there is assumed to be a potential of an arbitrary magnitude restricting the internal rotation. Previous to this, Sutherland and Dennison[1] have calculated the frequencies of the nondegenerate vibrations upon the assumption that forces between distant H atoms can be neglected, and

1 Sutherland and Dennison, Proc. Roy. Soc. A148, 250 (1935).