

Fluorescence Spectrum of Am³⁺ in LaCl₃

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Citation: *The Journal of Chemical Physics* **24**, 1115 (1956); doi: 10.1063/1.1742710

View online: <http://dx.doi.org/10.1063/1.1742710>

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phase, as did earlier work for the α phase within this pressure range.¹² However we find a strong temperature dependence for the pressure coefficient which, in the vicinity of Benisek, Kloseberg, and Kricheldorf is evidence that the variation of intermolecular bonding with intermolecular distance is an important factor in both the pressure and the temperature dependence of the measured frequency. Our measurements in turn give the following coefficients (in cm^{-1} per 10^3 psi, all α -D-D; α and β phases, $2.0 \text{ m}^\circ\text{C}^{-1}$; α and γ phases, $1.3 \text{ m}^\circ\text{C}^{-1}$; α phase - $0.5 \text{ m}^\circ\text{C}^{-1}$; γ phase $\rightarrow 0.1 \text{ m}^\circ\text{C}^{-1}$).

Work is continuing on these measurements, and we x-ray and neutron-scattering single crystal analysis of the structure is in progress in that laboratory.

¹Work done in the South African State Institute Laboratory and supported by the U. S. Air Force through the Office of Scientific Research of the Air Research and Development Command.

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Infrared Spectra of Polyethylene and Long Chain α -Paraffin

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OBservations of the infrared spectra of some highly crystalline, unbranched polyethylene and long chain α -paraffin, together with an examination of the rather meagre literature on this subject, indicate that several very unusual assignments exist.

According to the usual interpretation of the very long paraffin- α crystal spectrum at the end of a methyl bearing a methyl group lamellae with F_2 , the infrared spectrum should exhibit C-H stretching bands at 2915 , 2850 and 2820 cm^{-1} and C-H_2 rocking bands at 720 and 710 cm^{-1} all having perpendicular vibrations with respect to the crystal chain axis. In addition there should occur a single C-H_2 wagging band and possibly a C-H_2 twisting band slight of parallel vibrations. The perpendicular bands have all been assigned unambiguously and after no difficulty.¹ However, an unusual band can reasonably be assigned as a further mode. Four bands are observed^{2,3} at the angles being the C-H_2 wagging lamellae in crystals, namely at 1380 , 1360 , 1370 , and 1380 cm^{-1} . The first three must be due to the overlapping part of the polyethylene since their intensity increases very greatly upon melting and they are absent in the spectra of very long α -paraffin which form perfect crystals. This is very clearly indicated in the spectra of amorphous and crystalline polyethylene was observed by M. H. Hull and shown in the paper by Nichols.⁴ The remaining band at 1360 cm^{-1} is due to the asymmetric deformation mode of the terminal methyl groups. The possibility of overlapping here is excluded, since the spectrum of a very long chain unbranched polyethylene shows no absorption at this wave length.

The apparent absence (or extremely low intensity) of the C-H_2 wagging lamellae in polyethylene is quite unexpected for the following reason. In both the wagging and rocking modes of vibration, the direction of the low carbon bending vibrations is perpendicular to the chain. If the low carbon bending vibrations are perpendicular to the chain, it follows that the change in dipole moment for the wagging vibration would be nearly equal to that for a rocking vibration of the same amplitude. The same applies to the C-H_2 wagging mode in polyethylene. The same applies to the C-H_2 rocking mode in 720 cm^{-1} , using the formula $(\mu) = \frac{q}{4\pi\epsilon_0} \frac{d}{r^2}$ where q is the effective frequency in cm^{-1} and r is the

distance, would be surprising if the rocking vibration intensity were more than an order of magnitude greater than that of the wagging mode. Since the observed spectrum indicates that the discrepancy is more than this the lamellae must be considered unimportant.

The measurements of a parallel absorption band which are attributed to C-H_2 twisting in α -paraffins however, since in the approximation of isolated molecules (considering the structure with the fine group rather than the coarse group, reference 1) this vibration is inactive and its intensity is expected to be very low.

Similar difficulty in the spectral interpretation of paraffin crystals arises in connection with the well-known band at 1460 cm^{-1} of irregular spacing, sharp absorption in the angle 1460 - 1500 cm^{-1} . These bands are found with considerable intensity in certain long chain α -paraffin and other crystals containing long C-H_2 sequences.⁵ They are also observed in α -paraffin crystals with greatly reduced intensity. These bands have been generally attributed to C-H_2 wagging and/or C-H_2 twisting.^{6,7} This hypothesis would seem to be untenable on the basis of the spectrum obtained by Cohn and Jones⁸ of a single crystal of α -paraffin acid wherein the strong, sharp 1460 - 1500 cm^{-1} band is observed a polarization, the same as the component of the C-H_2 rocking vibration at 720 cm^{-1} ; i.e., perpendicular to the crystal chain axis. This is parallel as would be expected for both the wagging or twisting mode.

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Fluorescence Spectrum of As^{133} in JcCl_4

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(Received February 21, 1957)

IT is now well established that β decays occur in the ground state configurations of atoms and ions of the actinide elements.¹

Fluorescence is well known in a number of actinide ions where it occurs because of the presence of f electrons. By analogy, one would expect to observe fluorescence in some actinide ions.

Fluorescence has not been observed in actinides or plutonium compounds.² We wish to report here the first observation of the As^{133} fluorescence spectrum.

Single crystals of JcCl_4 (m.p. 50°C) containing 0.04 (sample I) and 0.20 (sample II) mole percent As^{133} were grown by the Stockbarger method.

The fluorescence is self-excited at room temperature owing to the radioactivity of As^{133} . For the observation of the fluorescence spectrum however, a 1000 w As^{133} source lamp was employed. The spectrum was photographed on a Jarrel-Ash 21-ft. Wadsworth constant spectrograph using a 15000 lines/in. grating and a 100 μ slit with exposure times of 1 to 9 hr. The dispersion of the spectrum is 0.004 μ /mm. Spectra were taken at room temperature and at liquid-nitrogen temperature.

All of the lines observed in the fluorescence spectrum are listed in Table I together with their vibrational assignments. Lines marked with an asterisk indicate absorption energy with lines found in the absorption spectrum, and may be observed in spectrum taken from some certain electronic states in the f^6 level of the ground state multiplet. The As^{133} fluorescence spectrum shows several features which are in this respect from its energy f^6 . In the former, we have observed fluorescence arising from the relatively low-lying excited electronic levels whereas in the latter fluorescence is observed only from the very lowest-lying electronic levels. There are two ground-state multiplets.

TABLE I. Fluorescence spectra of Ac^{228}Ac in LiCl .

No.	Wavelength (Å)	Intensity	No.	Wavelength (Å)	Intensity
1	4280	11	4320
2	4300	12	4340
3	4320	13	4360
4	4340	14	4380
5	4360	15	4400
6	4380	16	4420
7	4400	17	4440
8	4420	18	4460
9	4440	19	4480
10	4460	20	4500

The Ac^{228}Ac fluorescence spectrum is different to still another way. The line sum of 4285 Å and 4322 Å are observed only at one temperature while they are very strong. They disappear completely at 77°K.

Most of the line sum could be the same because even are observed only at 77°K.

An attempt has been made to raise out as far as possible effects owing to backscattering or artificial absorption. The substance (Ac^{228}Ac) was given a final purification by ion exchange from concentrated HCl solution using a Dowex-50 column. No backscattering or artificial absorption was found in either of the samples by double spectroscopic analysis.

The fluorescence spectra obtained from samples I and II were identical in every respect except that sample I had 100% more line which could be identified as Th^{232}Ac fluorescence line when they were compared exactly with that of the Pr^{140} standard line found in the LiCl starting material.

We are in the process of studying the photochemical properties of the fluorescence line in an aid to an interpretation of the spectrum.

A search is being made for the fluorescence of Pr^{140} .

We wish to acknowledge the skilful purification of Ac^{228}Ac by Dr. J. C. Holmwood. We thank the Health, Chemistry Group for the design and construction of neutron protection equipment. One of us (D.M.G.) wishes to thank Dr. G. T. Rothberg for making it possible for him to spend a year at the Radiation Laboratory.

This work was performed under the auspices of the U. S. Atomic Energy Commission at the University of California Radiation Laboratory.

University of California, Radiation Laboratory, Berkeley, California, Contract No. W-7406-ENG-48.

D. M. G. is indebted to the Atomic Energy, Oak Ridge-Yale Joint Company, Oak Ridge, Tennessee, for the use of the cyclotron.

Dr. G. T. Rothberg is indebted to the Atomic Energy, Oak Ridge-Yale Joint Company, Oak Ridge, Tennessee, for the use of the cyclotron.

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Raman Spectra of Liquid and Solid Hydrogen*

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(Received March 14, 1969)

THE Raman spectrum of liquid hydrogen was observed by McLennan and McLeod.¹ Their results showed that the spectrum in the liquid is very low quantum resolution, and that the rotational and vibrational Raman spectra differ only slightly, if at all, from those of the gas. However, a more precise knowledge of the rotational constants for the condensed phases is required in the interpretation of the complex pattern recently observed in the infrared absorption spectrum of the liquid and solid.² The Raman spectrum of the solid has therefore been investigated and the spectrum of the liquid re-examined.

A short Raman tube of conventional design was equipped vertically a 600 μm hole above the surface of liquid hydrogen in a

vertical Pyrex crystal. The tube was irradiated by a water-cooled helical mercury lamp surrounding the crystal and coated with Mg ; the scattered light was directed through the top of the crystal by a mirror and lens arrangement. By controlling the boiling of the liquid helium with a heating coil, the hydrogen could be maintained as a liquid or a solid within the few degrees of the boiling point for periods of several hours. The spectrum was photographed on Kodak 103 m-O film with a two-point plus spectrograph giving a wavelength linear dispersion of 65 cm^{-1} per mm at 4450 Å.

Spectrograms were obtained with normal hydrogen and with pure parahydrogen prepared by the method of Bygones and Stewart.³ In normal hydrogen the $Q(1)$ and $Q(2)$ rotational lines were observed by $\text{Hg } 4077, 4078, 4450$, and the $Q(1)$ line centered by $\text{Hg } 4451$ was observed; the $Q(1)$, $Q(2)$, and $Q(3)$ lines of the vibrational band were not seen. In parahydrogen the $Q(1)$ rotational line and the $Q(2)$ line were observed. The data, summarized in Table I, are average values from three spectrograms obtained with

TABLE I. Rotational constants of normal and para- H_2 .

Line	Normal		Parahydrogen		Parahydrogen	
	Wavenumber (cm^{-1})	Intensity	Wavenumber (cm^{-1})	Intensity	Wavenumber (cm^{-1})	Intensity
$Q(1)$	4451.0	100	4451.0	100	4451.0	100
$Q(2)$	4451.0	100	4451.0	100	4451.0	100
$Q(3)$	4451.0	100	4451.0	100	4451.0	100
$Q(4)$	4451.0	100	4451.0	100	4451.0	100
$Q(5)$	4451.0	100	4451.0	100	4451.0	100

* The rotational constants were measured for the gas temperature, and 4451 cm^{-1} for the $Q(1)$, 4451 cm^{-1} for the $Q(2)$, and 4451 cm^{-1} for the $Q(3)$ rotational lines of the liquid and solid.

rotational lines varying from 20 μm to 4 μm . The frequencies of the Q -lines were measured by a computer using an iron absorption spectrum; the rotational constant was found to agree exactly measured an microphotometer trace. Half-widths were observed from an intensity calibration of the plate with a stepped slit. The Raman spectra for the low-pressure gas were taken from a high-dispersion study by Christy.⁴

It is assumed that there is no change in the rotational constants in passing from normal to parahydrogen, as shown to be indicated by the only common line, $Q(1)$, line. The vibrational lines in normal gas band might be used to determine constants B_0 , B_1

TABLE II. Rotational constants of H_2 obtained from Raman data.

Phase	B_0 (cm^{-1})	B_1 (cm^{-1})	B_2 (cm^{-1})
Gas	4451.0	4451.0	4451.0
Liquid	4451.0	4451.0	4451.0
Solid	4451.0	4451.0	4451.0

and if the results are given in Table II along with the values for the gas calculated by a partial procedure. The constants for the liquid and solid are even in the literature within the accuracy of the determination. It appears to be well established that B_1 in the condensed phases is 10-20% smaller than in the gas. A proportion of the rotational constants is also needed; it is indicated, however, that the B_2 value is slightly greater in the condensed phases.

An interesting feature of the results is the different half-widths obtained for the 3- μm Q -lines. In all cases the Q -lines have a half-width indistinguishable from the spectral slit width ($\sim 2 \text{ cm}^{-1}$). The rotational lines, on the other hand, have half-widths of about 20 cm^{-1} in normal hydrogen. These observations are in accordance with the conclusions of Christy, Welch, and Herzberg⁴ that for normal hydrogen in the liquid and solid phases the rotational lines have very wide lines broadening as compared with normal gas.