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MONITORING OF DOPANT AND IMPURITY CONCENTRATIONS IN LIQUID ARGON BY INFRARED SPECTROSCOPY

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ABSTRACT:

We discuss applications and advantages of liquid phase infrared spectroscopy as a technique for monitoring dopant and impurity concentrations in liquid argon. The use of IR spectroscopy to detect contaminants in liquid argon is demonstrated. Gas and liquid phase spectra of ethylene and allene in argon are presented and compared. Absorption coefficients have been obtained for the principal peaks. The technique may be used to analyze a wide range of substances in cryogenic solution.

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1. Introduction

Infrared (IR) absorption spectroscopy may be used to detect molecular solutes dissolved in noble liquids [1,2]. It has therefore been suggested as a technique for monitoring the concentrations of dopants and impurities in noble liquid ionization media [3,4]. Conventional IR spectroscopy is performed with gaseous samples. Numerous advantages obtain, however, when liquified samples are analyzed [1,2,3]. First, the number density of solute molecules in a liquified sample is two to three orders of magnitude higher than it is in a gaseous sample of the same composition. Sensitivity to number concentration two to three orders of magnitude better than for gaseous samples therefore results for liquified samples, using the same optical path length. Second, molecular rotation is suppressed in cryogenic solutions. The IR spectra of substances in cryogenic solution are correspondingly simplified. Rotational spectral structure disappears, and the remaining vibrational peaks are smoother, more defined, and easier to measure and integrate. Moreover, the vibrational peaks appear at approximately the same wavenumber locations in gas and liquid phases, so that the large amount of existing data obtained from gaseous samples remains relevant for the qualitative analysis of liquid samples.

As part of our research into the use of doped liquid argon calorimetry in detectors for the Large Hadronic Collider, we aim to adapt IR spectroscopy techniques to the analysis of doped liquid argon solutions. We envision several applications of the technique:

- Monitoring of contaminant concentrations. IR spectroscopy allows impurities to be identified one-by-one, yielding information on the sources of liquid contamination. Many common contaminants of noble gases have spectral features in the medium-infrared region [5]. In particular, electronegative substances such as freons may easily be detected [3].

- Precise measurement of dopant concentrations. Ionization characteristics and electron mobilities in doped liquid argon depend strongly on the concentration of dopant.

-Studies on the maximum solubilities and radiolysis products of dopants.

To demonstrate that dopant concentrations in noble liquids may be determined by the use of IR spectroscopy, we have collected spectra of two potential dopants for liquid argon, ethylene and allene, and measured the absorption coefficients of their principal spectral peaks.

2. Experimental methods

A Bruker IFS-66 FT-IR spectrometer with a spectral resolution of 0.25 cm^{-1} was used to collect the spectra. The IR beam was obtained from a medium-infrared Globar source and received by an external, liquid nitrogen-cooled mercury-cadmium-telluride detector. Spectra were collected and analyzed using OPUS/IR version 1.2 software [6].

Samples were analyzed in a cryogenic cell with volume of 1.00 liter. The cell was originally designed to be combined with a detector used to study the ionization characteristics and electron mobilities of doped liquid argon solutions [7], so that IR analysis of the solutions could be performed *in situ*. For the present studies, however, the cell was detached from the detector, surrounded by 25 layers of aluminized Mylar and mounted inside a vacuum cryostat of its own. A copper tube through which liquid nitrogen could be circulated was wrapped around the cell. The pressure and temperature of the sample inside the cell could be monitored via a pressure gauge at the top and a thermocouple at the bottom. Samples could be stirred using a magnetic agitator mounted underneath the cryostat and a teflon-coated stirring bar inside the cell. The design of the sample cell is illustrated in Fig. 1.

The optical path length of the cell was 16.8 cm. In passing through the cell and its cryostat, the test beam traversed a total of four KRS-5 (thallium bromoiodide) windows of exposed diameter 2.5 cm and thickness 0.6 cm [8]. These windows were mounted in stainless steel and Teflon assemblies, and sealed on the interior side with a double ring of indium wire.

Gas and liquid phase samples of ethylene and allene in argon with solute number densities of 2.2, 5.6, 11, 17, and $22 \cdot 10^{16}$ molecules/cm³ were analyzed. These densities correspond to number concentrations of 1, 2.5, 5, 7.5, and 10 ppm in the liquid. An additional ethylene point was taken at $3.9 \cdot 10^{16}$ molecules/cm³ (1.75 ppm). The ethylene stocks from which samples were prepared were of N35 purity and prepared by the supplier in number concentrations of 0.5, 0.2, 0.1, 0.05, and 0.01% in argon N46. Allene stocks were of N20 purity and prepared by the supplier in number concentrations of 5, 2, 1, and 0.5% in argon N46. All stocks were calibrated by the supplier to within 2% error. Undiluted ethylene N35 and allene N20 were also used. Argon N46 was used as the solvent gas to make up the liquid volume [9].

Gas spectra were collected with the cell filled with the argon-ethylene or argon-allene stock at a pressure corresponding to the desired solute number density. The preparation of the liquid samples was much more involved. Before each measurement, the system was evacuated to a pressure of $\leq 2.5 \cdot 10^{-5}$ mbar and kept under vacuum for 12 to 16 hours. Liquid nitrogen was first circulated through the cell for about four hours to cool the cell to near liquid argon temperature. A reference spectrum was taken with the cell still evacuated. Argon gas was then allowed to flow through a mass flow meter and into the cell. The gas was introduced at the bottom of the cell. When the cell was about 1/3 full, the flow of argon was diverted through a calibrated volume containing the stock mixture at a known pressure. The dopant was thus swept into the cell and liquified with the remainder of the argon. Filling in this manner proceeded for approximately five hours with the dopant in the cell, so that the mixture was allowed sufficient time to reach homogeneity. Solvation of the dopant could be assisted using the magnetic agitator at the bottom of the cell. The cell was filled to a level completely covering the windows, corresponding to a liquid volume of 0.42 liter. The argon flow was then discontinued, the flow of liquid nitrogen through the cell was reduced, and the pressure inside the cell was allowed to stabilize at about 1 bar. About 15 spectra were then collected over a period of about one hour. During this time, the pressure in the cell, which was modulated by increasing or decreasing the nitrogen flow, varied between 0.85 bar and 1.05 bar, corresponding to a temperature interval of about 85.5-87.5 K. Temperature variations

over this interval were found to affect the absorbance measurements by only ± 1 -2%. Nevertheless, the spectra used in the analysis were all taken when the pressure was 1.0 bar.

3. Results and discussion

3.1. *Spectrum of liquid argon*

Since the reference spectra were taken with the cell evacuated, absorbance features due to contaminants of the solvent gas (argon N46) appear in the collected spectra. A spectrum of pure liquid argon is presented in Fig. 2. The two peaks at 2341 and 664 cm^{-1} arise from sample contamination by CO_2 . Particulate water suspended in the liquid gives rise to the features distributed about 3100 cm^{-1} and below 900 cm^{-1} . The small feature at 1304 cm^{-1} is most likely evidence of contamination by a halocarbon impurity such as CF_4 . The concentrations of these impurities were observed to differ from bottle to bottle. Other investigators have observed similar features in the spectra of liquid argon [3].

Integrations of the pure liquid argon spectra between the limits used for the later evaluation of the absorption coefficients of ethylene and allene yielded negligible absorbances. For the ν_7 peak of allene (1391 cm^{-1}), however, the limits of integration had to be chosen carefully in order to exclude the feature characteristic of CF_4 at 1304 cm^{-1} from the integrals.

3.2. *Spectra of ethylene and allene in liquid argon*

Gas and liquid phase transmission spectra of ethylene in argon are compared in Figs. 3a and b. The solute number density is $1.7 \cdot 10^{17}$ molecules/ cm^3 in both spectra. Assignments of the principal peaks to vibrational modes are suggested on the figures. These assignments have been obtained from refs. [10,11,12].

In the gas spectrum, the most prominent bands (ν_{11} , $\nu_7 + \nu_8$, ν_{12} , and ν_7) consist of narrow vibrational peaks bracketed by shoulders of rotational structure. Though the central vibrational peaks of ν_{11} , $\nu_7 + \nu_8$, and ν_{12} are less prominent than that of ν_7 in the gas spectrum, the heights of these peaks are enhanced more with the collapse of rotational structure in the liquid spectrum, as comparison between Figs. 3a and b demonstrates. The rotational structure of ν_7 is clearly resolved in the gas spectrum, as can be seen from the blow-up of ν_7 in Fig. 3c. The simplification of the spectrum in liquid phase can be clearly seen in this figure. The rotational peaks disappear in the liquid spectrum, and the remaining vibrational peak is clearly defined, though broader than the central vibrational peak of the gas spectrum.

Gas and liquid phase transmission spectra of allene in argon are compared in Figs. 4a and b. As in Fig. 3, the solute number density is $1.7 \cdot 10^{17}$ molecules/cm³ in both spectra. The assignments suggested on the figures have been obtained from [12].

The ν_6 , $2\nu_{10}$, and ν_7 bands of allene appear as broad double peaks in the gas spectrum. As seen in Fig. 4b, these collapse into sharper, more pronounced single peaks in the liquid spectrum. Smaller peaks which may contribute to the broad bands of the gas spectrum also become visible in the liquid spectrum. The ν_{10} band in the gas spectrum is characterized by rotational structure but lacks a central peak. The magnification of this band in Fig. 4c shows the distribution of rotational lines in the gas band giving way to a single, smooth peak in the liquid spectrum.

For both gases, the peak positions in the liquid spectra differ only slightly from those in the gas spectra. For ethylene, the average absolute displacement of the liquid peaks from the central maxima of the gas bands is about 3 cm⁻¹. Since the gas bands of allene lack central maxima, this displacement is harder to judge. As seen for the ν_{10} band in Fig. 4c, however, the positions of the liquid peaks correspond well with the approximate centers-of-gravity of the gas bands.

3.3. Absorption coefficients

The integrated absorbance of a spectral feature is defined by the relation:

$$A = -\int \ln (T_\nu) d\nu, \quad (1)$$

where A is the integrated absorbance (in this work, in cm^{-1}), and T_ν is the observed signal transmission at wavenumber ν (cm^{-1}). The relationship between the concentration of a given substance and the integrated absorbance of one of its spectral features is approximately given by:

$$A = \rho l Q; \quad Q = \int \sigma(\nu) d\nu, \quad (2)$$

where ρ (molecules/ cm^3) is the number density of solute molecules in the sample, l (cm) is the optical path length, $\sigma(\nu)$ ($\text{cm}^2/\text{molecule}$) is the cross section of the solute molecule for absorption of a photon of wavenumber ν , and Q (cm/molecule) is the integration of this cross section over the wavenumber interval of the feature. Q is referred to as the absorption coefficient of the feature. We note that the physical significance of Q is limited and depends on the limits of integration chosen and the technique used to perform the integral.

Our measurements of the absorption coefficients for the principal peaks of ethylene and allene are listed in Tables 1 and 2. The positions of the peak maxima in liquid phase and the limits used for the integration of each peak are also given in these tables. We used identical limits of integration for gas and liquid phase spectra to allow comparison between the values of Q_{gas} and Q_{liquid} . The limits were chosen so that for the spectrum of the gas phase sample with the highest concentration, no part of the feature of interest would be excluded from the integral. Spectral features were integrated relative to a straight line connecting the points on the spectra at the limits of integration.

It is interesting to compare the values of Q_{gas} and Q_{liquid} for each dopant. For ethylene, the gas and liquid phase values differ by only a few percent on average. This finding is consistent with the observations

of other investigators, who have noticed that gas and liquid phase absorption coefficients typically differ by $< 10\%$ [13]. For allene, however, we found the liquid phase values to range from 50 to 75% of their gas phase counterparts.

Comparing the values of Q obtained for each sample concentration allowed us to verify the consistency of our results. For all of the gas samples and for the liquid samples of concentration ≥ 2.5 ppm, the results were highly consistent.

For liquid samples of concentration < 2.5 ppm, some difficulties were experienced with the absorbance measurements. For ethylene, the absorbances of the four prominent peaks are plotted as functions of concentration in Fig. 5. The lines on this figure represent least square fits to the points with concentrations ≥ 2.5 ppm. At and above this concentration, all points lie on or very close to the fitted lines. Below this concentration, the absorbances of all four peaks seem to tend towards a nonzero value as concentration decreases. A similar plot is presented for allene in Fig. 6. Again, the lines have been fitted only to the points at concentration ≥ 2.5 ppm. For the one point taken with a sample concentration below 2.5 ppm, lower absorbances were measured than would agree with the rest of the data.

These effects can be attributed to errors in estimating the zero of absorbance. At high sample concentrations, such errors are negligible in comparison with the absorbances of the peaks, but as the peak absorbances themselves approach zero, the effects become pronounced. Because of these difficulties, we judged the measurements taken at sample concentrations < 2.5 ppm to be unreliable. We therefore excluded these measurements from the averages by which we obtained the values of Q_{liquid} presented in Tables 1 and 2.

We believe we can rule out the possibility that any experimental error in the concentrations of our samples explains the observed behavior. To confirm that no solute was transferred from sample to sample, we analyzed a sample of pure liquid argon after making a run at high concentration, and found no traces of dopant. The consistency of the results at higher concentrations indicates that the transfer of the

dopant to the cell was complete and that complete solvation of the dopant was achieved. Stirring the samples with the agitator had no effect. The maximum solubilities of ethylene and allene in liquid argon have been estimated to be orders of magnitude higher than the concentrations of our samples [14], and could not therefore have influenced our sample concentrations.

We estimate that our results are accurate to within $\pm 10\%$. As an index of the reproducibility of the data, the statistical errors associated with each value of Q are presented in the tables.

4. Conclusions

We have conducted studies on the IR spectroscopy of doped liquid argon solutions, with the aim to develop a purity and dopant concentration monitor for ionization detectors. The ability to detect impurities in liquid argon by IR spectroscopy has been confirmed. The technique may as easily be applied to the purity analysis of other cryogenic liquids, such as liquid xenon.

Gas and liquid phase spectra of ethylene and allene in argon have been collected and compared. The disappearance of rotational structure and the enhancement of vibrational peaks in liquid phase spectra have been demonstrated. The positions of the absorbance peaks were found to differ slightly in gas and liquid phase spectra.

Gas and liquid phase absorption coefficients have been obtained for the principal peaks of ethylene and allene. For the ethylene peaks, the values of Q_{gas} and Q_{liquid} were observed to be similar, while for the allene peaks, the values of Q_{liquid} ranged from 50 to 75% of the corresponding values of Q_{gas} . Due to difficulties in establishing the zero of absorbance, the measurements made with liquid samples of concentration < 2.5 ppm were not reliable. The consistency of the data obtained from gas samples and from liquid samples at concentrations ≥ 2.5 ppm was good.

We obtained the presented values of Q_{liquid} by analyzing samples of concentrations between 2.5 and 10 ppm. Using a suitable path length, however, these values may be applied to the analysis of samples over a wide range of concentrations.

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Figure captions

- Fig. 1:** Design of the sample cell. The liquid nitrogen heat exchanger and magnetic agitator are not shown.
- Fig. 2:** Transmission spectrum of liquid argon N46.
- Fig. 3:** Transmission spectra of ethylene: **a.** in gas phase, **b.** in liquid argon. Assignments to vibrational modes have been obtained from [10,11,12]. Detail of the ν_7 peak in both gas and liquid phases is shown in **c.** The solute number density is $1.7 \cdot 10^{17}$ molecules/cm³ in all spectra.
- Fig. 4:** Transmission spectra of allene: **a.** in gas phase, **b.** in liquid argon. Assignments to vibrational modes have been obtained from [12]. Detail of the ν_{10} peak in both gas and liquid phases is shown in **c.** The solute number density is $1.7 \cdot 10^{17}$ molecules/cm³ in all spectra.
- Fig. 5:** Absorbance vs. concentration relations for the prominent peaks of ethylene in liquid phase. The lines are fitted to the points with concentrations ≥ 2.5 ppm. The absorbances plotted for the ν_7 peak have been divided by 10.
- Fig. 6:** Absorbance vs. concentration relations for the prominent peaks of allene in liquid phase. The lines are fitted to the points with concentrations ≥ 2.5 ppm. The absorbances plotted for the ν_6 and ν_{10} peaks have been divided by 10.

Table 1: Absorption coefficients of ethylene

Peak location (cm^{-1})	Integration limits (cm^{-1})	Q_{gas} ($\text{cm}/\text{molec.}$)	Q_{liquid} ($\text{cm}/\text{molec.}$)	Modes thought to contribute to Q
2984.0	3040-2930	$7.06 \pm 0.09 \cdot 10^{-19}$	$7.20 \pm 0.04 \cdot 10^{-19}$	ν_{11}
1885.6	1945-1835	$3.28 \pm 0.03 \cdot 10^{-19}$	$2.71 \pm 0.02 \cdot 10^{-19}$	$\nu_7 + \nu_8$
1439.2	1500-1385	$7.50 \pm 0.06 \cdot 10^{-19}$	$8.12 \pm 0.11 \cdot 10^{-19}$	ν_{12}
949.5	1100-825	$6.59 \pm 0.08 \cdot 10^{-18}$	$6.37 \pm 0.08 \cdot 10^{-18}$	ν_7

Table 2: Absorption coefficients of allene

Peak location (cm^{-1})	Integration limits (cm^{-1})	Q_{gas} ($\text{cm}/\text{molec.}$)	Q_{liquid} ($\text{cm}/\text{molec.}$)	Modes thought to contribute to Q
1957.4	2045-1880	$3.81 \pm 0.04 \cdot 10^{-18}$	$1.84 \pm 0.07 \cdot 10^{-18}$	ν_6
1681.1	1725-1635	$5.38 \pm 0.05 \cdot 10^{-19}$	$2.96 \pm 0.08 \cdot 10^{-19}$	$2\nu_{10}$
1391.1	1435-1325	$4.63 \pm 0.03 \cdot 10^{-19}$	$3.45 \pm 0.14 \cdot 10^{-19}$	ν_7
838.9	955-690	$6.62 \pm 0.28 \cdot 10^{-18}$	$5.12 \pm 0.15 \cdot 10^{-18}$	ν_{10}

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6