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BHABHA ATOMIC RESEARCH CENTRE

STUDIES ON THE SEPARATION OF HYDROGEN ISOTOPES AND SPIN ISOMERS BY  
GAS CHROMATOGRAPHY

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K. K. Pushpa and K. Annaji Rao  
Radiation Chemistry & Chemical Dynamics Division

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# Studies on the Separation of Hydrogen Isotopes and Spin Isomers by Gas Chromatography

*K.K. Pushpa and K. Annaji Rao*

## **Abstract:**

Separation and analysis of mixture of hydrogen isotopes has gained considerable importance because of various applications needing different isotopes in lasers, nuclear reactions and tracer or labelled compounds. In the literature gas chromatographic methods are reported using columns packed with partly dehydrated or thoroughly dehydrated alumina/molecular sieve stationary phase at 77°K with helium, neon and even hydrogen or deuterium as carrier gas. In the present study an attempt is made to compare the chromatographic behaviour of these two stationary phases using virgin and 'Fe' doped form in partly dehydrated and thoroughly dehydrated state, using helium, neon, hydrogen and deuterium as carrier gas. The results of this study show that helium or neon carrier gas behave similarly giving broad peaks with some tailing. Sharp symmetric peaks are obtained with hydrogen or deuterium carrier gas. This is attributed to large hold up capacity for H<sub>2</sub> or D<sub>2</sub> at 77° K in these materials as compared to helium or neon. Spin isomers of H<sub>2</sub> or D<sub>2</sub> are separated on 'Fe' free stationary phases, though 'ortho' H<sub>2</sub> and HD are not resolved. Using a combination of 'Fe' doped short column and plain alumina column, both maintained in dehydrated form, the effect of 'Fe' doping on thermal equilibrium of ortho/para forms at 77° K is clearly demonstrated.

## Introduction:

In recent times the use of hydrogen isotopes in various applications like nuclear chemistry involving heavy water, tritium labelling and laser gas mixtures, has made it necessary to separate and analyse the isotopic composition. Different applications require specific isotopes and therefore there is a need to know the composition and purity. Gas chromatography is a simple and elegant technique for the separation and analysis of gaseous mixtures. This technique has been used for the separation and analysis of hydrogen isotopes. The gas chromatographic separation has been carried out using columns packed with alumina [1,4,7,9,14], molecular sieve [2,3,5,6] or etched capillary glass [8] column at temperatures below 120° K [12]. The columns have to be specially prepared and conditioned. Only helium or neon can be used as carrier gas because of low temperature. Alternatively hydrogen or deuterium has been used as carrier gas monitoring HD/D<sub>2</sub> or H<sub>2</sub>/HD [3,6,10,15,16] while T<sub>2</sub>/HT/DT is monitored using tritium counters [14]. These techniques are used regularly in one mode or the other depending on the isotopes of interest, though the situation gets very complex if all combinations are present and their analysis is required.

These methods are being used for quite some years, though certain experimental results have not yet been understood. Peak shape and resolution are found to be better if the stationary phase is doped with paramagnetic material like 'Fe' [1], treated with carbon dioxide [4] and also partially hydrated [5,9]. Helium or neon carrier gas gives broad and somewhat tailing peaks. Hydrogen or deuterium carrier gas gives fast separations with good resolution and sharp symmetric peaks [3,6,10]. The equilibrium concentrations of ortho- and para- isomers in H<sub>2</sub> and D<sub>2</sub> being significantly different at various temperatures [13] and the equilibrium between the two forms is attained very slowly in the absence of a catalyst (paramagnetic material like 'Fe') the peaks tend to be broad while with 'Fe' doped matrix, the equilibrium is attained quickly and better peaks are obtained.

The gas hold up volume in these solid stationary phases at low temperature (77° K) and the affinity for absorbed components play an important role in the separation and elution. Faster elution with better peak shape and resolution are obtained at lower carrier flow rate when the stationary phase is partly dehydrated in case of alumina [1,4,9], molecular sieve 5A or 4A with 'Fe' doping [5].

In order to get a better insight into these aspects, studies are carried out using alumina and molecular sieve 5A in plain form, 'Fe' doped form both in dehydrated and partly dehydrated condition as column stationary phase with helium, neon, hydrogen and deuterium as carrier gas. Experiments have also been conducted using combination of two columns containing 'Fe' doped molecular sieve 5A and plain alumina in dehydrated condition to evaluate the effect of 'Fe' doping. Using two columns – alumina and 'Fe' doped alumina in series with helium carrier gas peaks corresponding to para-H<sub>2</sub>, ortho- H<sub>2</sub>, HD and D<sub>2</sub> have been obtained on injecting a mixture of H<sub>2</sub>/HD/D<sub>2</sub> [11]. The gas hold up capacity of the materials used as stationary phases with respect to helium, hydrogen and deuterium have been measured. The results of this study are given here.

### **Experimental:**

A laboratory built gas chromatograph with facility to keep the column immersed in liquid nitrogen (77° K) in a 5 litre Dewar flask (capable of maintaining the liquid nitrogen level within 1 to 2 cms for 3 to 4 hours) and provided with thermal conductivity detector is used. The carrier gas flow system is maintained leak tight end to end. While changing the carrier gas the unit is first equilibrated at room temperature with the gas flowing for some time through the column and the outlet. The outlet is then plugged pressurizing the system and then the column is slowly cooled down by immersing it in liquid nitrogen. After the system has attained the equilibrium pressure, the outlet plug is removed allowing the gas to flow and stabilize. During this process special care is taken to see that no air or moisture is sucked back into the column (this can cause contamination or

column end blockage). This exercise is very important since the carrier gas is changed frequently and also the hold up capacity of the column particularly in the case of H<sub>2</sub> or D<sub>2</sub> is very large, causing the pressure increase as the column warms up to room temperature or causing partial vacuum when cooled to 77° K. A schematic of the unit is given in Figure 1. As these experiments are intended to check separation characteristics under different conditions, no special effort is made to enhance detector sensitivity. The detector bridge current is maintained in the range of 200 to 250 mA. Same set up is used for all the experiments.

The gas samples used are normal hydrogen from cylinder, synthetic mixture of H<sub>2</sub>/HD/D<sub>2</sub> in approximately 2:1:2 ratio and D<sub>2</sub> (~96%D<sub>2</sub>, 4%HD and trace H<sub>2</sub>) from cylinder. Helium and neon used for carrier gas are from M/s Matheson, USA and hydrogen (99%+) from M/s Indian Oxygen. Deuterium is obtained from (electrolysis of D<sub>2</sub>O and filled under pressure in gas cylinder) Heavy Water Division, Bhabha Atomic Research Centre.

The experiments are carried out with three main objectives : (A) The effect of various carrier gases on the separation of hydrogen isotopes using columns packed with alumina or molecular sieve 5A in plain or 'Fe' doped form in partially dehydrated or fully dehydrated condition. (B) The effect of 'Fe' doping on the separation of spin isomers 'ortho' and 'para' and (C) The elucidation of 'Fe' doping effect on the ortho/para equilibrium using dual column technique.

(A) There are reports about using fully dehydrated or partially dehydrated stationary phases [1,3,4,5,7]. A comparative study of performance of molecular sieve 4A and 5A with 'Fe' doping has been reported by us [5]. In the present study only molecular sieve 5A and alumina are used. Alumina is doped with 'Fe' as reported earlier [1]. Partially dehydrated molecular sieve 5A (15% Fe) is prepared and packed in the column as per earlier report [5]. Complete dehydration of molecular sieve 5A column or 15% 'Fe' doped molecular sieve 5A column is done by heating it under nitrogen flow isothermally at 523° K for 6 hours and allowing it to cool to room temperature

in nitrogen flow and changing to the required carrier gas without exposing to air or humidity. Dehydration of alumina/alumina'Fe' is done under helium flow at 733° K for 20 hours and then cooling to room temperature in helium flow. The gas is changed to the required carrier gas without exposing the column to air or humidity. Partially dehydrated alumina 'Fe' is prepared as below. Completely dehydrated alumina 'Fe' is emptied out from the column, spread as a thin layer in a petri dish and kept in a closed humid container (closed desiccator with water instead of desiccant) to absorb moisture to saturation. It is then placed in air oven maintained at 383° K for one hour. At the end it is packed in the column with minimum exposure to air.

In the case of molecular sieve, a copper column of 3.8 m length x 2.5 mm i.d. is used. In the case of alumina a copper column of 1.8 m length x 2.7 mm i.d. is selected on the basis of preliminary experiments so that the separation of peaks for H<sub>2</sub>/HD/D<sub>2</sub> mixture in the partially dehydrated alumina 'Fe' column is comparable to that obtained with partially dehydrated molecular sieve 5A (Fe).

Gas hold up capacities in these columns at 77° K for helium, hydrogen and deuterium are determined as per the following procedure. At the end of the chromatographic runs with a particular carrier gas, the column outlet is connected to a length of flexible 1mm inner diameter tubing, with the other end dipping in a vessel containing water, letting gas to bubble through water. This outlet is then plugged and almost simultaneously the carrier inlet to the column is shut off. A gas holding jar filled with water is inverted over the plugged end of the tubing. The chromatographic column is slowly lifted out of liquid nitrogen allowing it to warm up, quickly removing the end plug to collect the evolved gas in the jar by downward displacement of water, till the pressure equilibrates to atmospheric pressure and column attains room temperature. The entire process of gas containment and collection is achieved by proper synchronization of the operations involved and the error is about  $\pm 2\%$ .

(B) Experiments to see the effect of 'Fe' doping on the separation of ortho- and para- hydrogen.

These experiments are performed using columns filled with 'Fe' doped alumina in partially dehydrated and fully dehydrated form, plain alumina in dehydrated form and with molecular sieve 5A dehydrated as well as with 'Fe' doped molecular sieve 5A in dehydrated and partially dehydrated form. Helium, hydrogen or deuterium is used as carrier gas. Though marginal separation between ortho- and para- D<sub>2</sub> is obtained with hydrogen carrier under these experimental conditions, this aspect is not pursued.

(C) The dual column technique using the combination of 'Fe' doped column and plain alumina column is used in this study on the basis of the results obtained in part (B). A 30 cm x 2.5 mm i.d. copper column filled with 'Fe' doped molecular sieve 5A in dehydrated condition is used either as a precolumn or post column as required. Plain alumina filled in 1.8m x 2.7 mm i.d. copper column and dehydrated, is used as the main separation column. The configuration used is shown in Figure 2 schematically. Both columns are maintained at 77° K. These experiments are aimed at providing experimental evidence for the catalytic role of 'Fe' in the stationary phase, inducing quick equilibrium between ortho and para isomers for the given temperature. When hydrogen at room temperature is injected to the system with D<sub>2</sub> carrier gas and 'Fe' doped pre-column followed by the alumina column, the isomers get equilibrated at 77° K first and pass on to the second column as single peak where they are separated into ortho- and para- components and elute as two peaks with intensity corresponding to equilibrium concentration at 77° K. However, when the 'Fe' doped column is positioned after the main column, the ortho- and para- isomers are separated as two peaks first and then enter the 'Fe' doped column and emerge as two peaks with intensity corresponding to equilibrium concentration at room temperature (~300° K).

## Results:

The gas hold up capacities of stationary phases used in the experiments are given in Table I. The hold up capacity for H<sub>2</sub> and D<sub>2</sub> in both alumina and molecular sieve is much more than helium, dehydrated molecular sieve showing a very large difference.

**Table I**

Gas hold up capacity of stationary phases in ml/gm

Gas	Alumina 'Fe' Part. Dehydrated	Alumina Dehydrated	Mol.Sieve 5A Dehydrated	Mol.Sieve 5A + 15% Fe, Dehydrated	Mol.Sieve 5A + 15% Fe, Part.Dehydrated
He	1.85	2.31	3.85	3.74	2.29
H <sub>2</sub>	8.86	10.6	50.2	10.32	3.94
D <sub>2</sub>	10.44	11.7	60.3	10.97	4.58

In case of all columns the separation behaviour with carrier gas helium and neon, are similar and no particular advantage is gained with neon except for sensitivity due to difference in thermal conductivities. Chromatograms obtained under various conditions are given in Figures 3, 4 & 5. Partly dehydrated 'Fe' doped alumina and 15% Fe doped molecular sieve 5A columns give comparable separation for H<sub>2</sub>/HD/D<sub>2</sub> (Figure 3a, 3b). In the case of dehydrated stationary phases, the peaks tend to tail heavily. Alumina 'Fe' column separates H<sub>2</sub>/HD/D<sub>2</sub> under dehydrated condition with poor peak shape (Figure 5b) in comparison to partly dehydrated form (Figure 5c). In contrast peaks are badly distorted in dehydrated Fe doped molecular sieve 5A (Figure 5a). Alumina in plain form gives separation for H<sub>2</sub>/HD/D<sub>2</sub> with poor resolution (Figure 4a) as compared to 'Fe' doped alumina (Figure 5b). The sample is not eluted out in plain dehydrated molecular sieve 5A.

Higher carrier flow is required to get the elution in dehydrated form as compared to partly hydrated form.

The chromatographic behaviour of these columns is very different with hydrogen or deuterium as carrier gas. The samples are eluted from the column quickly even in dehydrated molecular sieve 5A at low carrier flow rates. The peaks are symmetric, sharp with good resolution. Dehydrated columns give better separation compared to partly dehydrated columns. The chromatograms obtained with hydrogen carrier gas and deuterium carrier gas on different stationary phases are given in Figures 6,7,8 & 9. The peaks obtained with 'Fe' doped material and plain material in the dehydrated form show differences. With deuterium carrier gas, when hydrogen is injected on to dehydrated alumina or dehydrated molecular sieve 5A column two peaks are obtained (Figure 7b, 9d), the retention time of second peak matching with HD peak [1] (Figure 10b, 11b). The two peaks obtained with H<sub>2</sub> sample are attributed to para- and ortho- H<sub>2</sub> [3,7,15]. The peaks intensity is in the range of 1:2. Only single peak is obtained with 'Fe' doped dehydrated stationary phase on injecting hydrogen (Figure 9b) and HD if present is seen as a well resolved peak appearing after H<sub>2</sub> peak (Figure 9a). The behaviour is similar in the case of hydrogen carrier and deuterium injected as sample (Figure 6, 8). In the case of dehydrated alumina or molecular sieve 5A column the peak due to D<sub>2</sub> is seen as a combination of a main peak followed by a small shoulder (Figure 6b). The order of elution in case of ortho- D<sub>2</sub> and para- D<sub>2</sub> is reported to be ortho- first followed by para- D<sub>2</sub> [6, 7, 15]. The chromatograms (Figure 6b, 8b) illustrate these differences. The role of 'Fe' dopant in the quick attainment of ortho/para equilibrium is evident in the two sets of separations. In the absence of 'Fe' the column is able to separate the two isomeric forms since the absorption/elution rate is faster compared to exchange at 77° K while the exchange is faster in the presence of 'Fe' [1]. The equilibrium concentration of ortho- and para- isomers of hydrogen and deuterium at various temperatures below 300° K is given [13] in Table II

**Table II**Thermal Equilibrium Concentration of Ortho- and Para Isomers of H<sub>2</sub> and D<sub>2</sub> [13]

Temp	P-H <sub>2</sub>	O-H <sub>2</sub>	Temp	P-D <sub>2</sub>	O-D <sub>2</sub>
20 ° K	99.82	0.18	20 ° K	2.03	97.97
77 ° K	50.41	49.39	70 ° K	28.22	71.78
120 ° K	32.87	67.13	120 ° K	32.93	67.07
-	-	-	190 ° K	33.32	66.68
273 ° K	25.13	74.87	260 ° K	33.33	66.66
300 ° K	25.00	75.00	300 ° K	33.33	66.66

The results obtained with dual column experiments bring out clearly the role of 'Fe' dopant on the thermal equilibrium in ortho-/para- isomers. The sample of hydrogen injected on to the dehydrated 'Fe' doped molecular sieve 5A precolumn followed by dehydrated alumina column with deuterium carrier gas, will first get equilibrated to 77 ° K equilibrium concentration of ortho/para fractions and pass on to alumina as single peak. This peak is resolved into ortho- and para- fraction in this column and emerge as two distinct peaks with intensities in 1:1 ratio corresponding to 77 ° K. However, in the case where 'Fe' doped column is after the alumina column, the sample of hydrogen as injected is resolved into two peaks corresponding to the equilibrium concentration at room temperature by alumina and pass on to the post column as two distinct peaks and elute out as such with intensity ratio 1:3 corresponding to 300 ° K. The chromatograms obtained are given in Figure 10 & 11. Using hydrogen carrier gas and injecting H<sub>2</sub>/HD/D<sub>2</sub> sample under the dual column experiments with Fe doped molecular sieve 5A as post column, a peak due to HD followed by peak due to D<sub>2</sub> with a shoulder is obtained (Figure 11c). This is similar to the chromatogram obtained with single dehydrated alumina column (Figure 6b), the two peaks under D<sub>2</sub> being ortho- D<sub>2</sub> followed by para- D<sub>2</sub> as shoulder peak.

### Conclusion:

The separation of a mixture of H<sub>2</sub>/HD/D<sub>2</sub> at 77° K using 'Fe' doped alumina in dehydrated or partly dehydrated form as well as plain alumina in dehydrated form with helium and neon as

carrier gas show similar results. Partly dehydrated 'Fe' doped alumina gives better separation with less tailing and peak broadening as ortho/para separation is suppressed. In the case of dehydrated alumina with deuterium carrier gas good separation of ortho- and para- hydrogen is obtained, though ortho-hydrogen and HD are not separated.

In the case of molecular sieve 5A doped with 15% Fe, the chromatographic behaviour with helium and neon as carrier gas is similar with both partly dehydrated and dehydrated forms. The peaks tail very badly in the dehydrated form while separation is obtained with partly dehydrated form and is comparable to the separation obtained with partly dehydrated alumina 'Fe'. In contrast the components are not eluted on dehydrated molecular sieve 5A.

The gas hold up capacity for both hydrogen and deuterium is very high as compared to helium and the difference increases with dehydration, plain molecular sieve 5A showing the maximum difference in the dehydrated form. This is reflected in the chromatographic behaviour.

The behaviour of both alumina and molecular sieve 5A under hydrogen or deuterium as carrier gas is similar, with respect to both plain and 'Fe' doped forms. Apparently with hydrogen and deuterium as carrier the absorption sites which have strong affinity for H<sub>2</sub> or D<sub>2</sub> are already saturated and do not participate in the chromatographic process while with helium or neon these sites are not occupied and thus hold up H<sub>2</sub>/D<sub>2</sub> resulting in long retention times and tailing.

The result obtained with dual column experiment clearly elucidates the 'Fe' catalytic effect.

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## Legend for figures:

Figure 1 Schematic of the gas chromatograph

Figure 2. Schematic of the dual column mode

Details common to Figures 1 & 2:

1. Carrier flow inlet line
2. Fine flow control for TCD reference gas
3. Fine flow control for column
4. Injection port
5. Column outlet coupler
6. TCD (4 filament type)
7. Dewar for liquid nitrogen
8. Single column in place
- 8a Short precolumn\*
- 8b Regular column\*
- 9 Inter coupler for 8a and 8b

\*(Position of 8a and 8b are interchanged for the post column operation)

## Legend for chromatograms

Figure 3a Molecular sieve 5A + 15% Fe, 3.8m x 2.5mm i.d., partly dehydrated column, Helium carrier gas 30ml/mt – H<sub>2</sub>/HD/D<sub>2</sub> sample (1ml)

Figure 3b. Column same as in 3a, Neon carrier gas 60ml/mt - H<sub>2</sub>/HD/D<sub>2</sub> sample (60µl)

Figure 4a. Alumina dehydrated, 1.8m x 2.7mm i.d. column, Helium carrier gas 100ml/mt – H<sub>2</sub>/HD/D<sub>2</sub> sample (3ml)

Figure 4b. Column same as in 4a, Neon carrier gas 95ml/mt – H<sub>2</sub>/HD/D<sub>2</sub> sample (900 µl)

Figure 5a Molecular sieve 5A + 15% Fe, 3.8m x 2.5mm i.d. dehydrated, Neon carrier gas 120ml/mt, - H<sub>2</sub>/HD/D<sub>2</sub> sample (1ml).

Figure 5b Alumina (Fe), 1.8m x 2.7mm i.d. dehydrated, Helium carrier gas 75ml/mt - H<sub>2</sub>/HD/D<sub>2</sub> sample (600μl).

Figure 5c Alumina (Fe), 1.8m x 2.7mm i.d. partly dehydrated, Helium carrier gas 60ml/mt - H<sub>2</sub>/HD/D<sub>2</sub> sample (1ml).

Figure 6a Molecular sieve 5A + 15% Fe, 3.8m x 2.5mm i.d. Partly dehydrated, Hydrogen carrier gas 60ml/mt - H<sub>2</sub>/HD/D<sub>2</sub> sample (300μl)

Figure 6b Alumina dehydrated, 1.8m x 2.7mm i.d., Hydrogen carrier gas 60ml/mt - H<sub>2</sub>/HD/D<sub>2</sub> sample (700 μl).

Figure 6c Molecular sieve 5A + 15% Fe, 3.8m x 2.5mm i.d., Dehydrated, Hydrogen carrier gas 30 ml/mt - H<sub>2</sub>/HD/D<sub>2</sub> sample (400 μl).

Figure 7a Molecular sieve 5A + 15% Fe, 3.8m x 2.5mm i.d., Partly dehydrated, Deuterium carrier gas 60ml/mt - H<sub>2</sub>/HD/D<sub>2</sub> sample (200μl).

Figure 7b Alumina dehydrated, 1.8m x 2.7mm i.d. Deuterium carrier gas 60ml/mt – H<sub>2</sub> sample (800μl).

Figure 7c Molecular sieve 5A + 15% Fe, 3.8m x 2.5mm i.d. Dehydrated, Deuterium carrier gas 30ml/mt - H<sub>2</sub>/HD/D<sub>2</sub> sample (300μl).

Figure 8a Alumina (Fe), 1.8m x 2.7mm i.d. Dehydrated, Hydrogen carrier gas 60ml/mt - H<sub>2</sub>/HD/D<sub>2</sub> sample (600 μl).

Figure 8b Alumina (Fe), 1.8m x 2.7mm i.d. Partly dehydrated, Hydrogen carrier gas 37ml/mt – D<sub>2</sub> sample (500 μl).

Figure 8c Molecular sieve 5A, 3.8m x 2.5mm i.d. Dehydrated, Hydrogen carrier gas 120 ml/mt - H<sub>2</sub>/HD/D<sub>2</sub> sample (600μl).

Figure 9a Alumina (Fe), 1.8m x 2.7mm i.d. Dehydrated, Deuterium carrier gas 30ml/mt - H<sub>2</sub>/HD/D<sub>2</sub> sample (600μl).

Figure 9b Alumina (Fe), 1.8m x 2.7mm i.d. Dehydrated, Deuterium carrier gas 30ml/mt - H<sub>2</sub> sample (300μl).

Figure 9c Alumina (Fe), 1.8m x 2.7mm i.d. Partly dehydrated, Deuterium carrier gas 37ml/mt - H<sub>2</sub> sample (500μl).

Figure 9d Molecular sieve 5A, 3.8m x 2.5mm i.d., Dehydrated, Deuterium carrier gas 120ml/mt - H<sub>2</sub> sample (500μl).

Figure 10a Column I, Dehydrated Molecular sieve 5A + 15% Fe 30cm x 2.5mm i.d.

Column II, Dehydrated Alumina, 1.8m x 2.7mm i.d.

Deuterium carrier gas 40ml/mt - H<sub>2</sub> sample (300 μl).

Figure 10b Configuration as in 10a, Deuterium Carrier gas 40ml/mt - H<sub>2</sub>/HD/D<sub>2</sub> sample (800μl).

Figure 11a Column I, Dehydrated Alumina 1.8m x 2.7mm i.d.

Column II, Dehydrated Molecular sieve 5A + 15% Fe 30cm x 2.5mm i.d.

Deuterium carrier gas 40ml/mt - H<sub>2</sub> sample (500μl).

Figure 11b Configuration as in 11a, Deuterium carrier gas 40ml/mt - H<sub>2</sub>/HD/D<sub>2</sub> sample (500μl).

Figure 11c Configuration as in 11a, Hydrogen carrier gas 40ml/mt - H<sub>2</sub>/HD/D<sub>2</sub> sample (500μl).

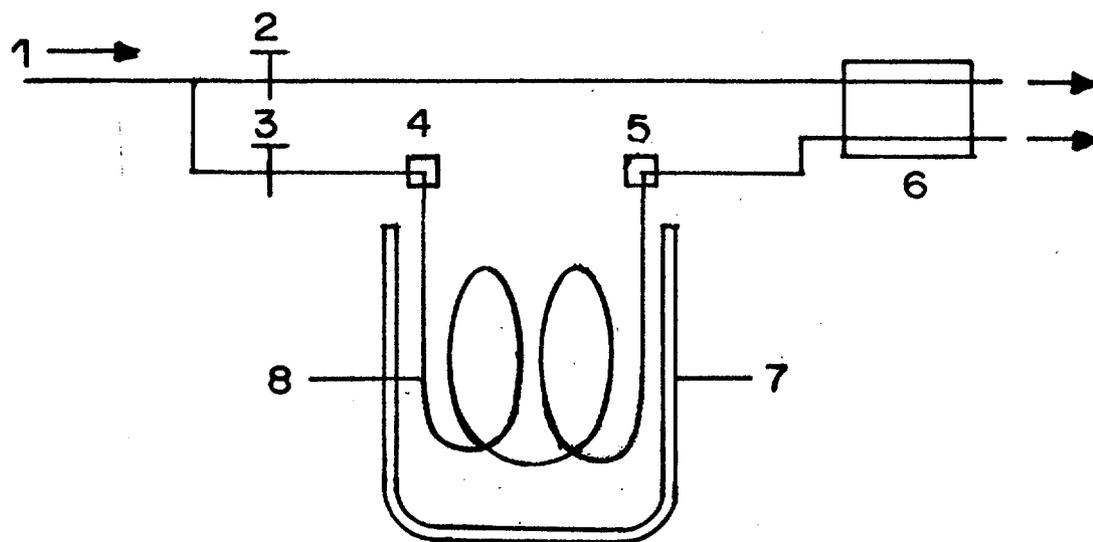


FIG. 1

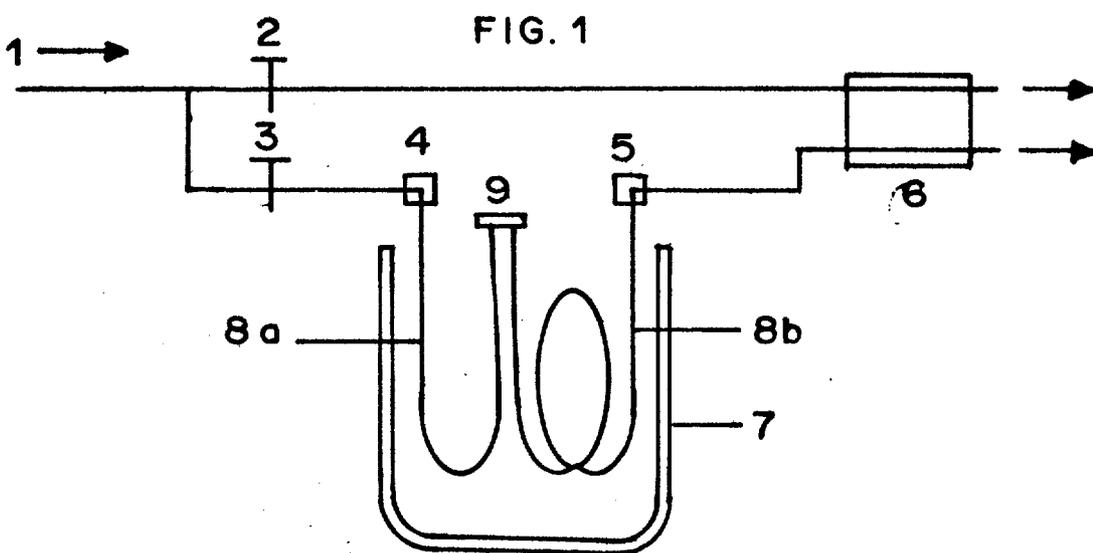


FIG. 2

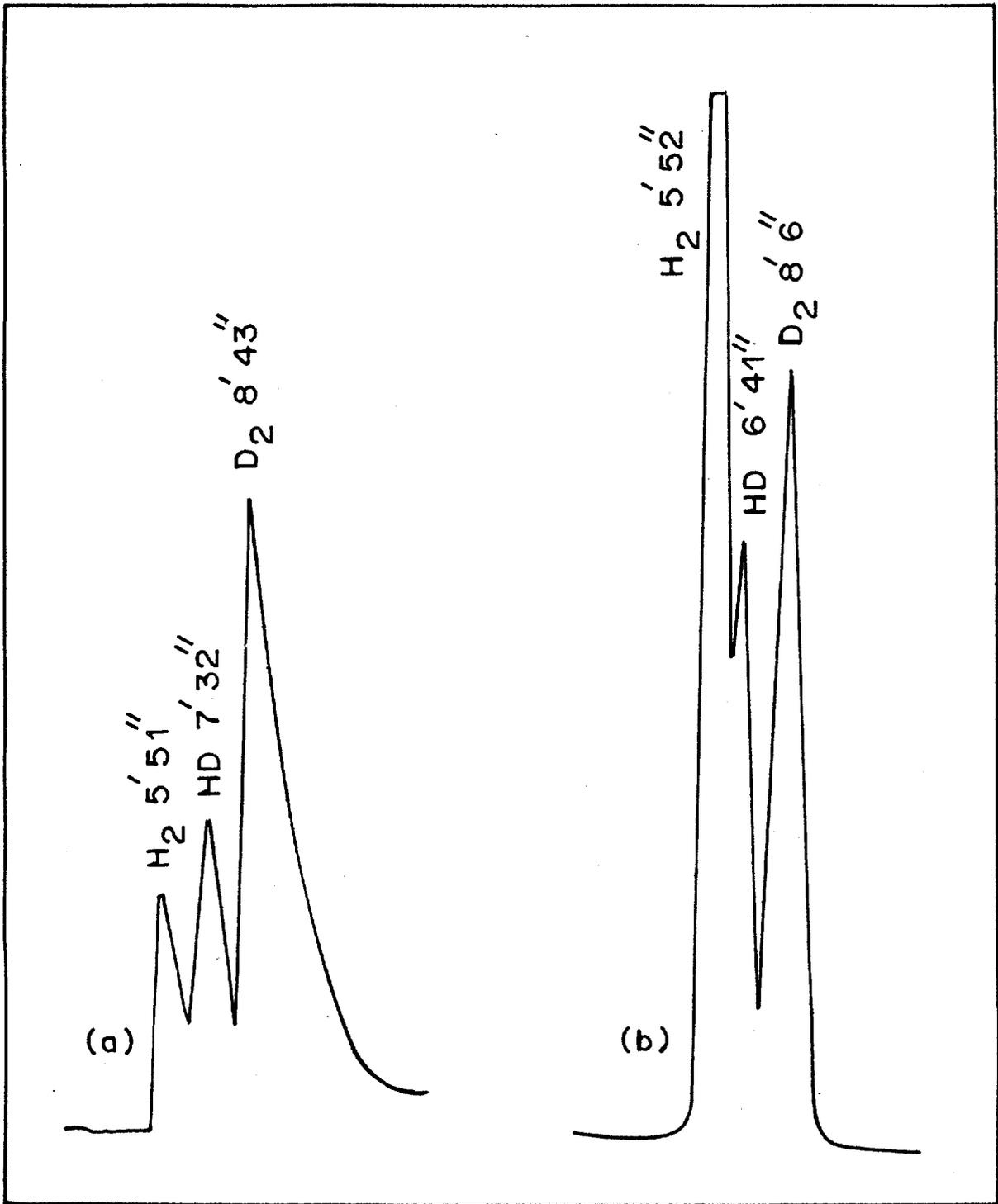


FIG. 3

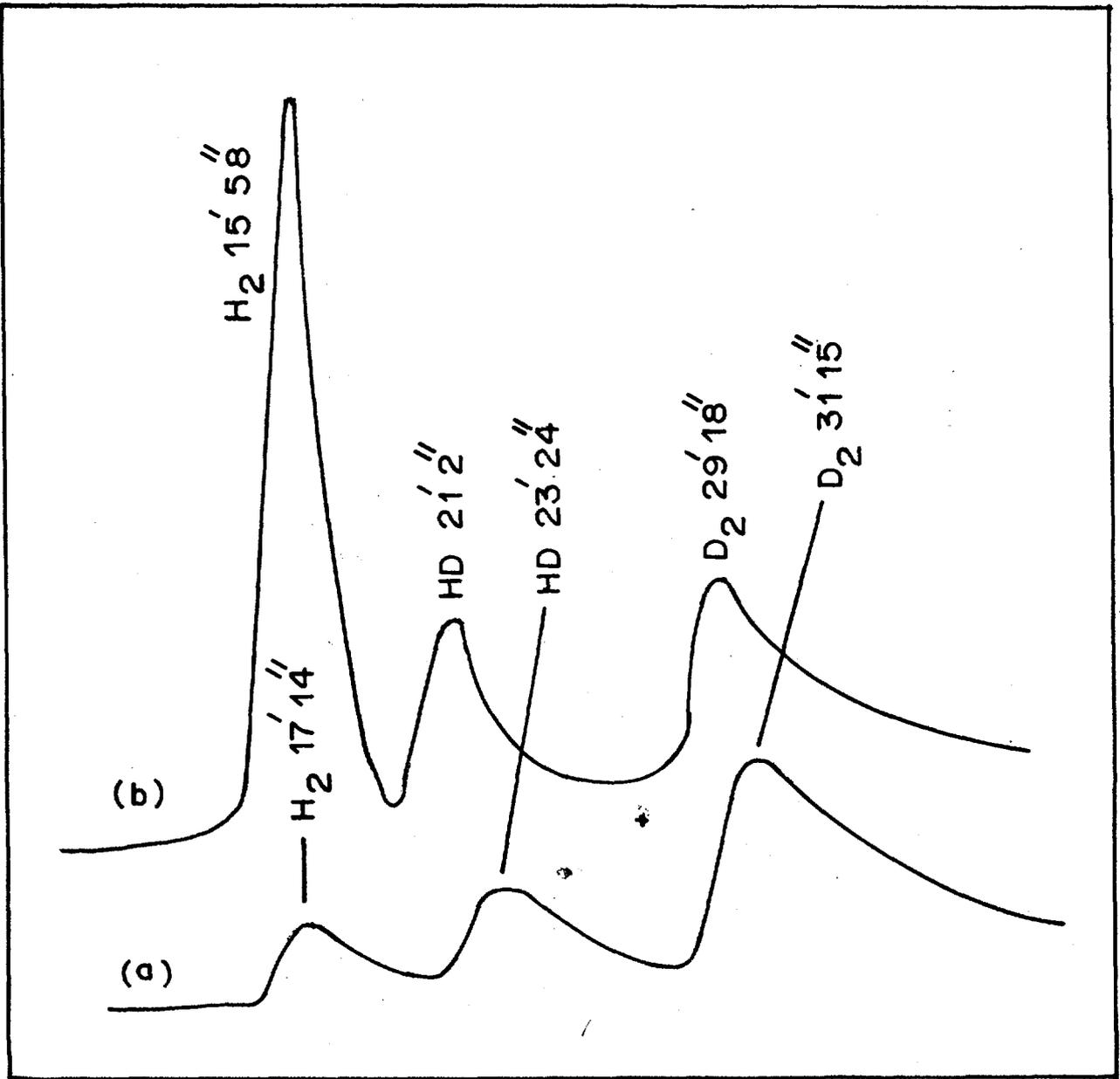


FIG. 4

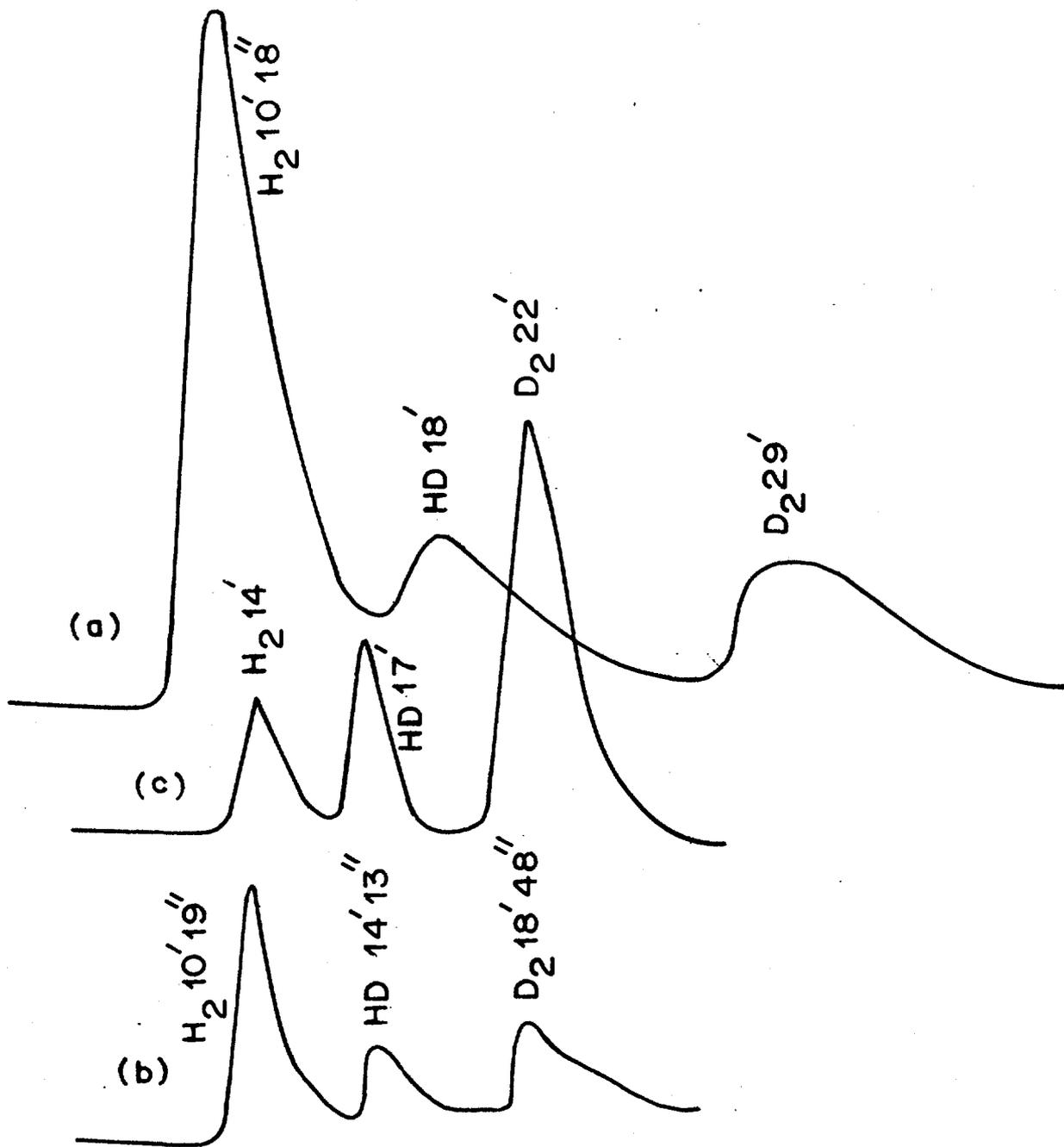


FIG. 5

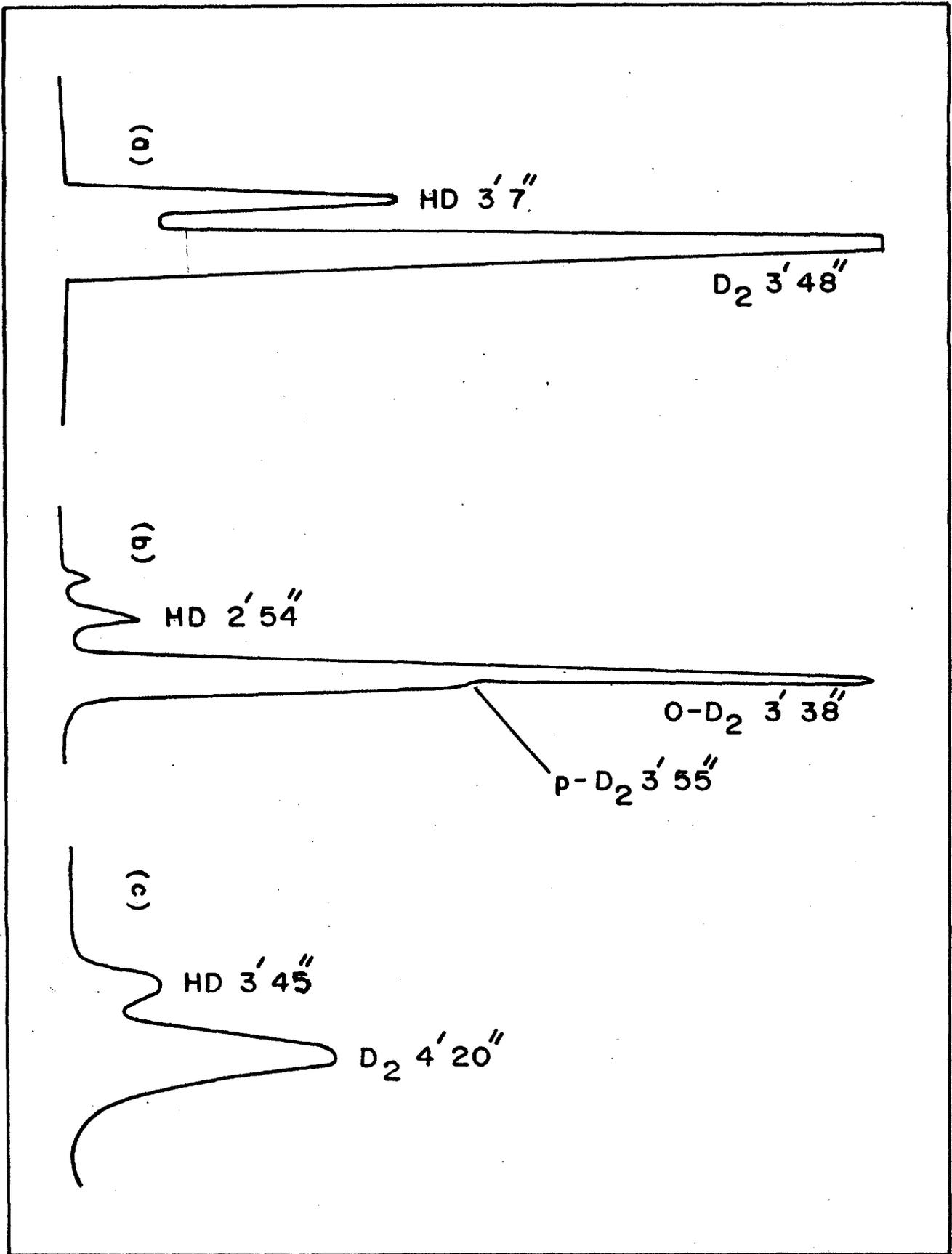
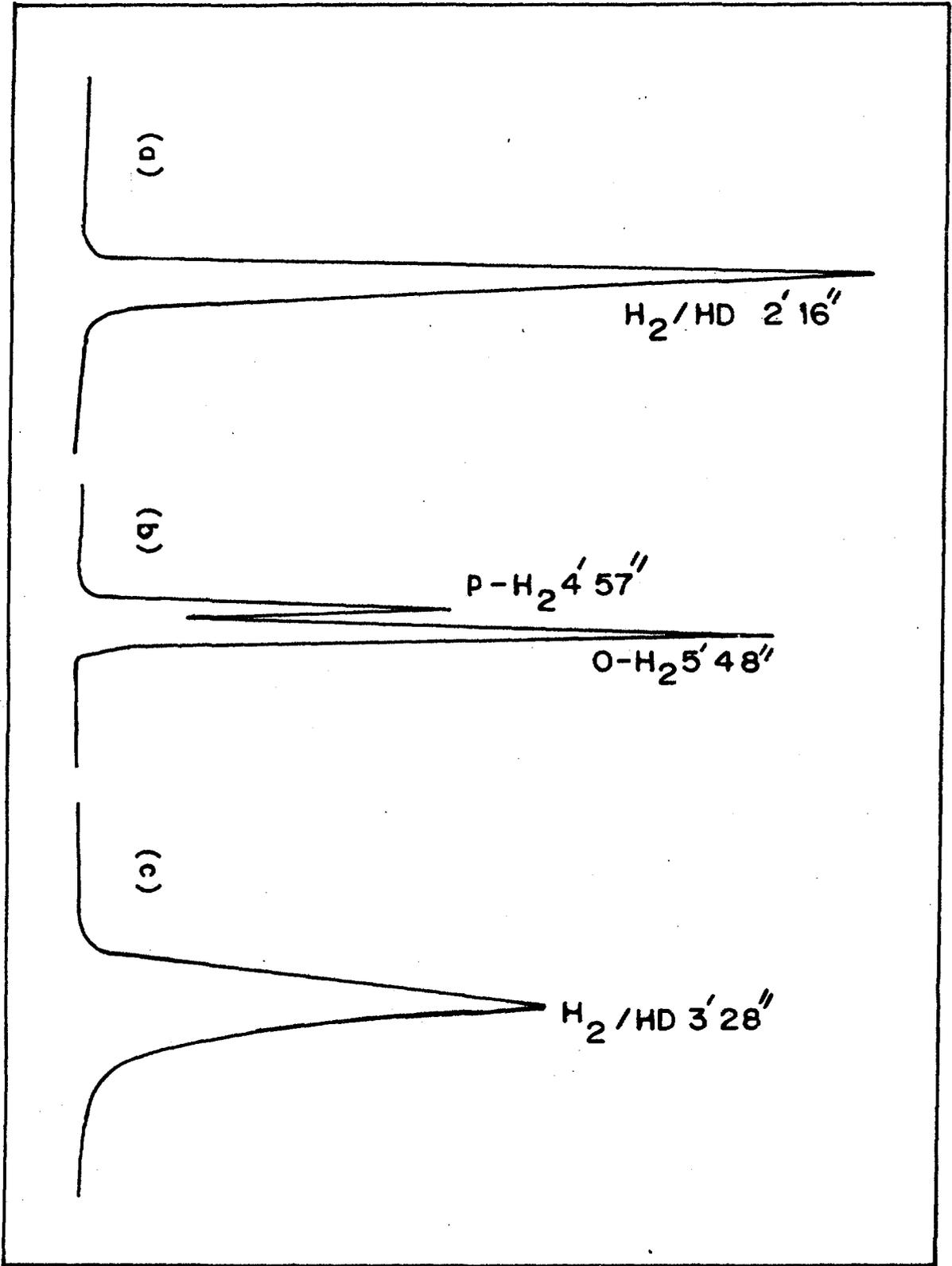


FIG. 6

FIG. 7



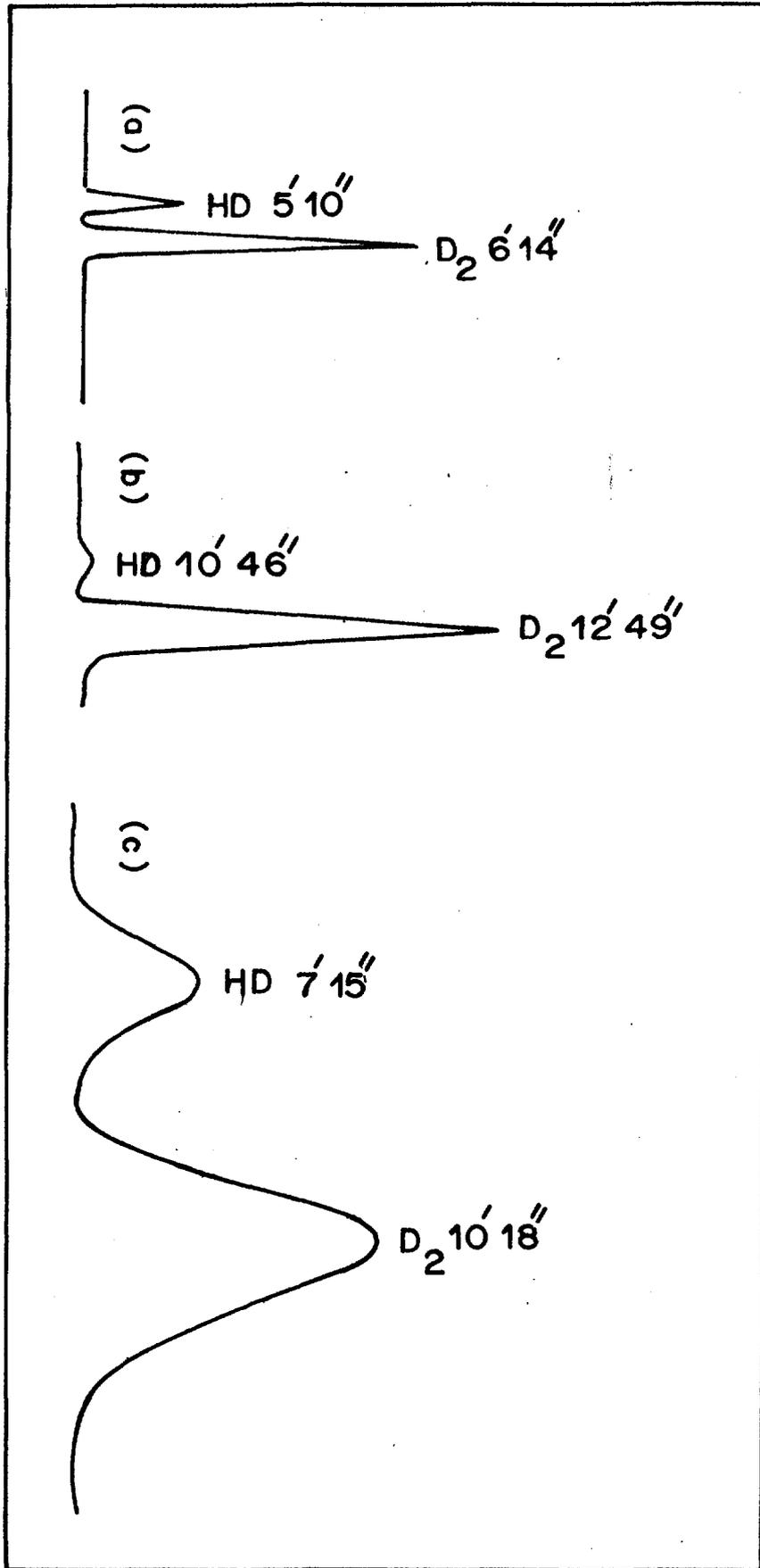
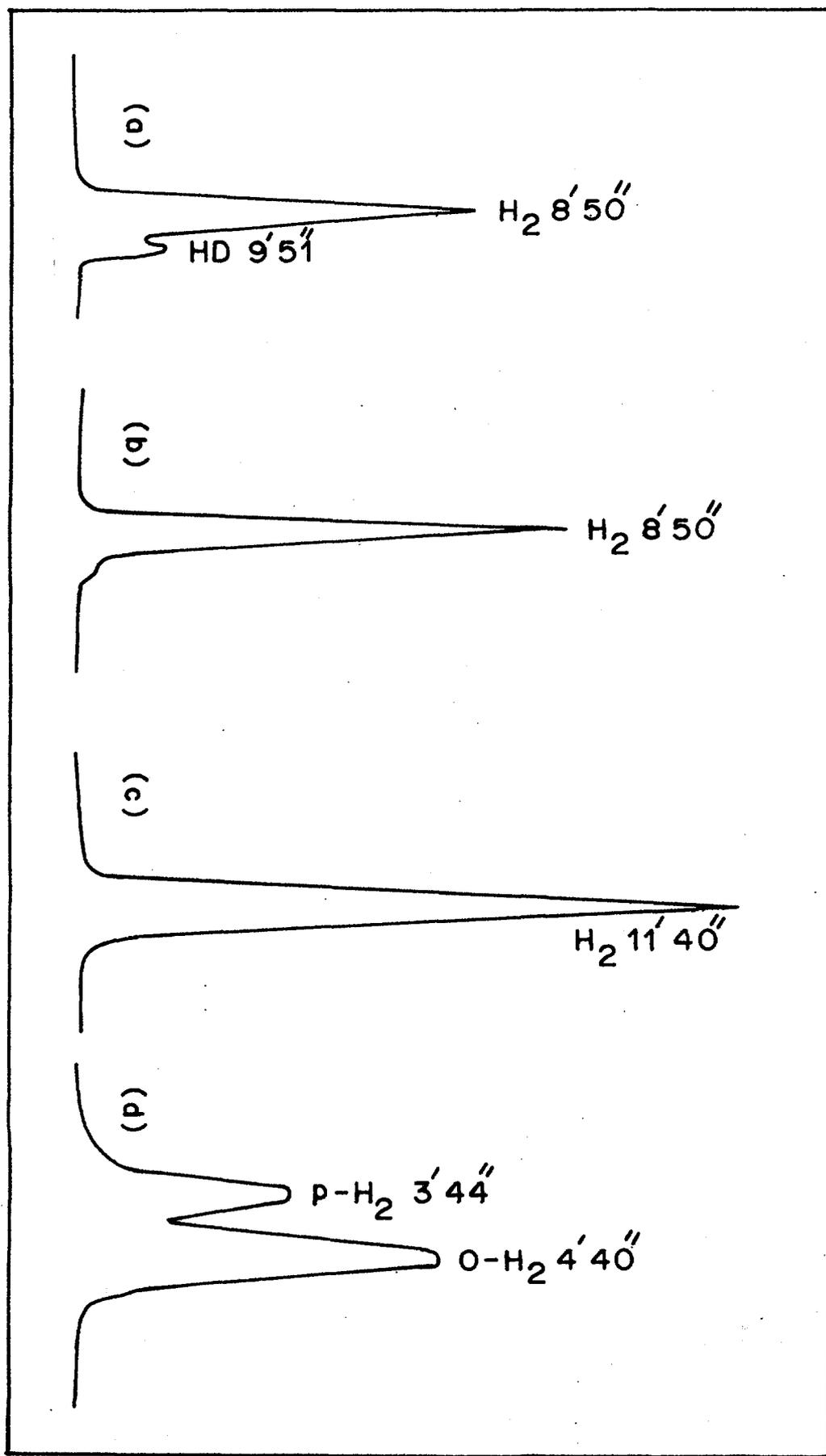


FIG. 8.

FIG. 9



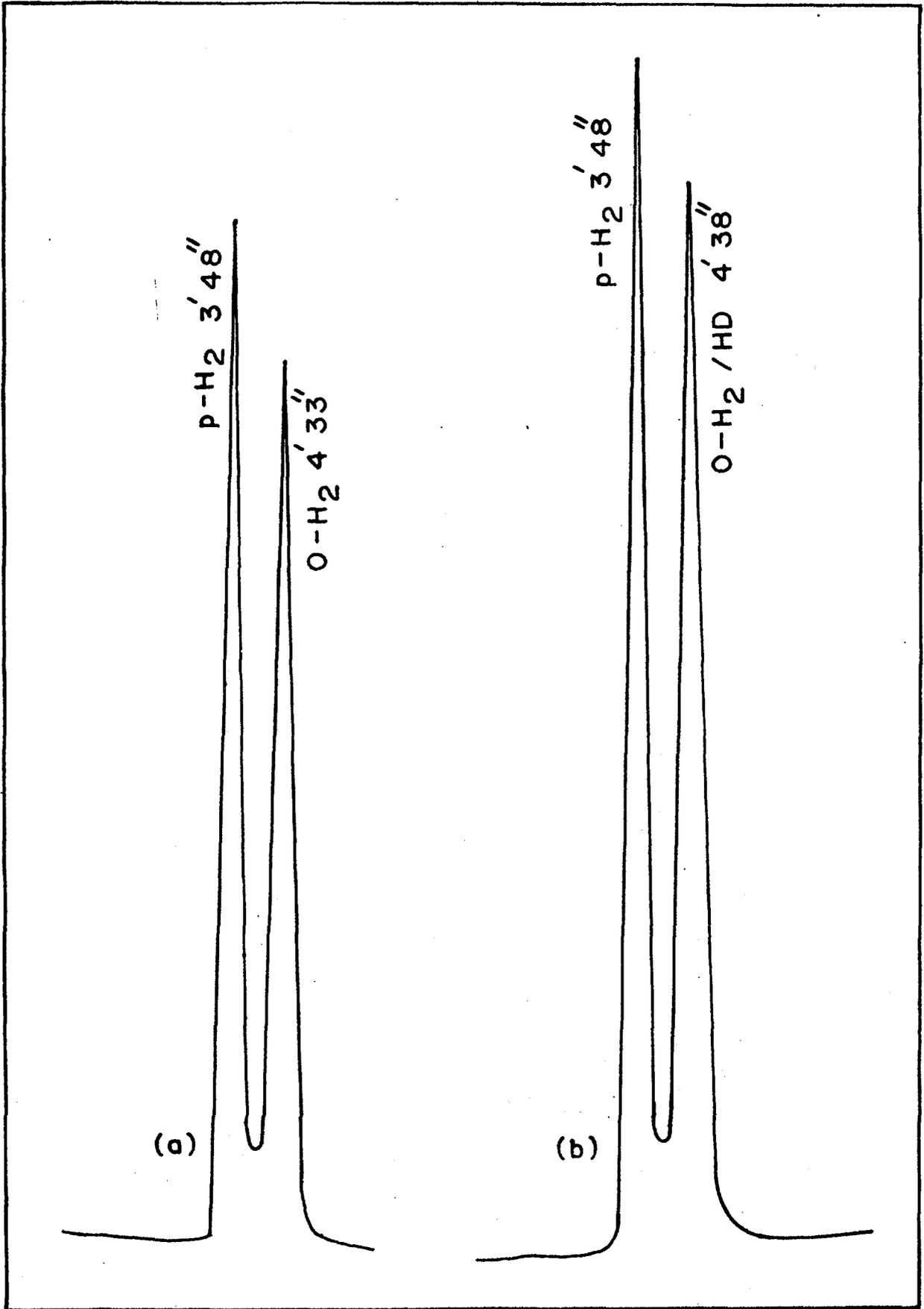


FIG. 10

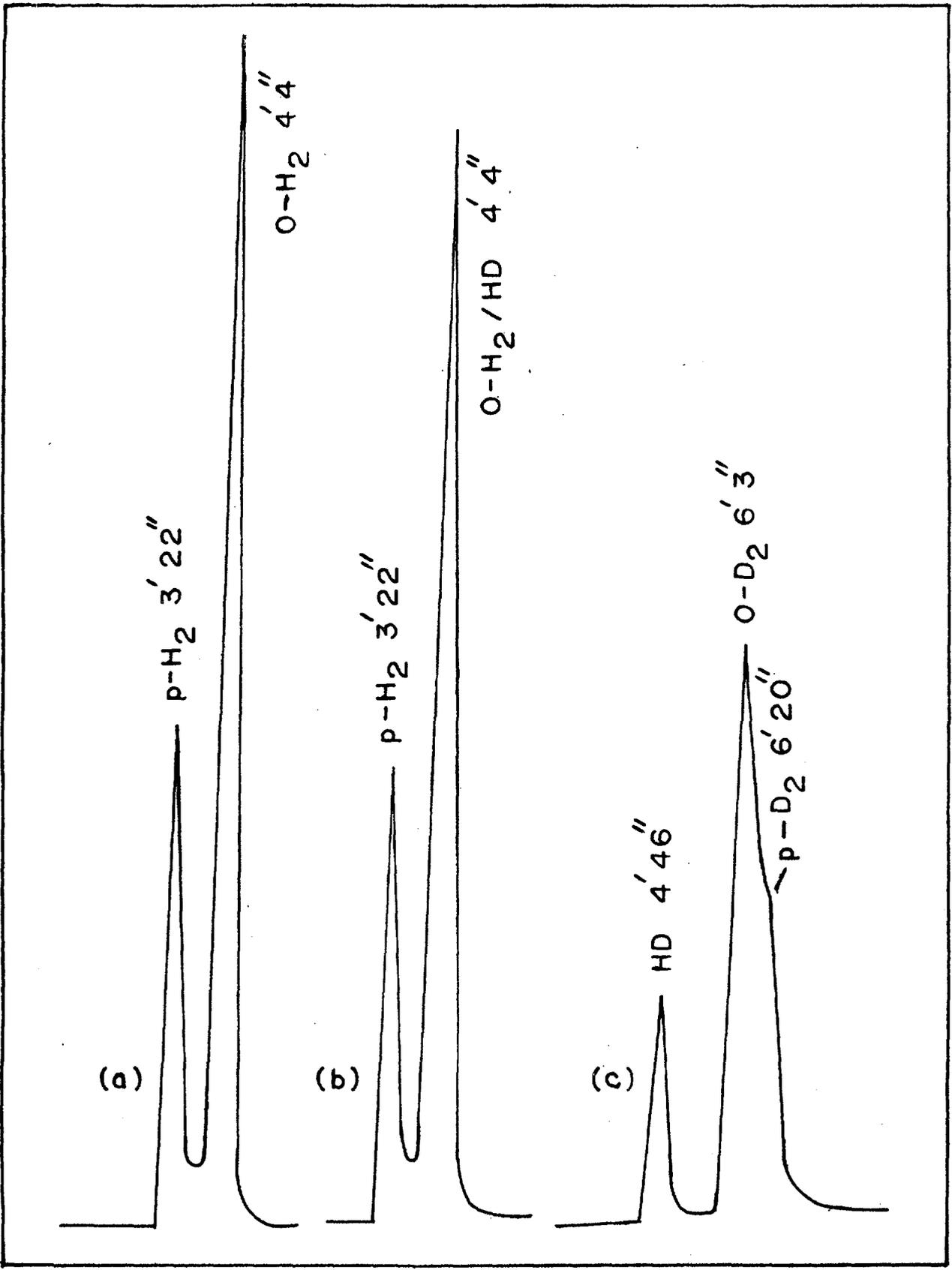


FIG. 11

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