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AND SOLID D-T

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INFRARED ANALYSIS OF LIQUID
AND SOLID D-T*P. C. Souers, E. M. Fearon, R. K. Stump,
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The composition of a liquid or solid deuterium-tritium mixture may be measured by collision-induced infrared spectroscopy. For T_2 , DT and D_2 , respectively, we measure the areas under the absorption peaks in the regions 76.75-80.19, 85.29-88.74 and 92.79-96.23 THz (2560-2675, 2845-2960 and 3095-3210 cm^{-1}). These areas are multiplied, respectively, by these isotopic sensitivities derived from quantum calculations: 1.000, 0.891 and 0.811. The resulting numbers are proportional to the molar composition. Nearly equimolar D-T samples show good agreement between mass and infrared spectroscopy. The large DT peak in enriched molecular DT over emphasizes D_2 in the infrared analysis, but these results may be corrected with the room temperature, mass spectroscopic D-to-T ratio.

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It is sometimes desirable to measure the mol percents of D_2 , DT and T_2 in a deuterium-tritium (D-T) solution in the liquid or solid state. The atomic composition may be determined by high resolution mass spectroscopy. The molecular-compositions, however, are those of room temperature, where the sample equilibrated before the analysis. Small amounts of HD and HT will not appreciably change in mixing and cooling to cryogenic temperatures, but the three major components could be quite different from the room temperature mix. This is especially true in enriched molecular DT mixes made for nuclear spin polarization experiments.¹

Infrared spectroscopy offers a non-destructive method of measuring the three major constituents in condensed D-T. The method works best for the just-frozen solid, where all the lines are sharp and the solid is too soft to crack. The liquid spectra are clear, but the lines are broader and overlap more. As the solid is cooled to 4 K, stress cracks appear, which, at the worst, make the sample opaque. Sometimes a crystal can be cooled to 4 K and retain an unflawed character.

Diatomic hydrogen molecules do not possess, even for HT, large permanent electric dipole moments. Only transient electric dipole moments are present when molecules interact. This produces a weak infrared absorption, which is called "collision-induced," because it is caused by molecular interaction. The infrared absorption increases as the square of the density, so that a good signal is obtained - from our 8-mm thickness of solid or liquid, whereas many meters would be needed for the dilute gas.

Because of the need for molecular interaction, all transitions giving rise to infrared absorption are double, i.e., they involve two molecules. The basic transition is the molecular vibration $v=0 \rightarrow 1$, which occurs on one of the molecules. Both molecules can have molecular rotational or phonon transitions in addition. Every transition, then, has six permutations, given the three hydrogens D_2 , DT and T_2 . This creates many lines whose overlap makes analysis difficult. Narrow single transitions may be had by Raman spectroscopy, which should be easier to analyze than infrared. However, a Raman spectrometer costs three to four times more than an infrared system.

We have previously described the use of infrared spectroscopy with the cryogenic hydrogens.^{2,3} We, therefore, move to the liquid example shown in Fig. 1 of 22 mol% T_2 -50% DT-28% D_2 , taken at a 1.9 THz/min ($63 \text{ cm}^{-1}/\text{min}$) scanning rate. The three hydrogens have different masses and their spectra fall at different vibrational frequencies. However, splittings occur because of transitions from the two rotational states of hydrogen: $J=0$ and $J=1$,⁴ where J is the molecular rotational quantum number. To this is added the complication of the six possible molecular interactions.

The best infrared peaks to use for quantitative analysis are the Q + S transitions, which are numbered in Fig. 1 and listed in Table 1.⁵ In this series, one of the molecules undergoes a rotational $J=\Delta 2$ transition. For Q + S(0), the transition is $J=0 \rightarrow 2$; for Q + S(1), it is $J=1 \rightarrow 3$. These peaks are directly proportional in area to the isotopes

giving rise to them, unlike others in the spectrum. Almost no $J=1$ DT exists in cryogenic D-T so that no $S_0(1)$ DT transitions are present in Table 1.

Each measurement region includes only four of the five $Q + S$ lines. If the regions were broader, we would run into some problems. For example, the $Q_1(0)$ DT peak at 82.02 THz (2736 cm^{-1}) falls just in front of peak number 5. The $Q_1(0,1)$ D_2 peak at 89.52 THz (2986 cm^{-1}) falls between peaks 9 and 10 in Fig. 1. The Q -phonon peak for DT is the broad bump between peaks 5 and 6. We do not know how to quantitatively treat either Q_1 peaks or Q -phonon peaks.

We need next a list of relative sensitivities of the infrared lines; for example D_2 peaks are inherently larger, for the same number of molecules, than T_2 lines. The theory of the peak intensities has been presented by Poll.⁶ The integrated absorption is proportional to the square of the sample density

$$A = \int \frac{1}{\nu} \ln \left(\frac{I_0}{I} \right) d\nu = a_1 \rho^2 + \text{higher order terms} \quad (1)$$

Here, ν is the frequency, I_0 the base line transmission intensity, I the intensity of the spectrum at the frequency ν , and ρ the density. The coefficient a_1 is proportional to the Clebsch-Gordon coefficient times the transition matrix elements. The former tells the strength of the transition type, i.e., whether it is a $S(0)$ or $S(1)$ transition. The second is specific to the particular isotope and transition. The matrix elements have been calculated by quantum mechanical methods by Wolniewicz.⁷

Table 1 lists the sensitivities of the various transitions in terms of the inverse of the various coefficients we have just considered. We set the $Q_1(0,1)T_2 + S_0(0)T_2$ transition equal to 1. The resulting numbers are multipliers, i.e., we multiply the actual peak areas by these numbers to obtain numbers proportional to mol fractions. The matrix element multiplier is multiplied by the Clebsch-Gordon multiplier (equal to 1 for $S_0(0)$ and $5/3$ for $S_0(1)$ transitions) to obtain the total multiplier.

We select three regions, containing almost completely $Q_1 + S$ peaks, to analyze for T_2 , DT and D_2 . These are, respectively: 76.75-80.19, 85.29-88.74 and 92.79-96.23 THz (2560-2675, 2845-2960, and 3095-3210 cm^{-1}). The average multipliers for the T_2 , DT and D_2 regions, β_6 , β_5 and β_4 , are 1.000, 0.891 and 0.811. The hydrogen species actually being measured in each region is the $Q_1(0,1)$ molecule.

We next measure the sample and an empty cell at cryogenic temperatures. Just before the $Q_1(0,1) T_2$ peak in the spectrum at 72.5 to 75.0 THz (2420 to 2500 cm^{-1}), there is a minimum. We raise or lower the baseline in %transmission space to match the spectrum at this point. We digitize the spectrum and integrate it over each region to obtain the peak areas A_6 , A_5 , and A_4 for T_2 , DT and D_2 , respectively. The mol percent of, e.g., D_2 would be

$$[D_2] = \frac{100\beta_4 A_4}{\beta_4 A_4 + \beta_5 A_5 + A_6} \quad (2)$$

where $\beta_6 = 1$ for T_2 . The other mol% are derived in a similar fashion. In Table 2, we list the compositions of several nearly equimolar D-T mixtures equilibrated at room temperature and measured by a

low resolution Varian CH5 magnetic sector mass spectrometer. The samples were cooled and measured by infrared spectroscopy within a few hours, before any appreciable change from the room temperature equilibrium could take place. The agreement between the two methods is good.

We have also used infrared spectroscopy to analyze enriched DT mixtures.¹ Figure 2 shows an example in the liquid state at 21 K. The D₂ peak (no. 12) rides on a large DT background, and a correction must be made by moving some apparent D₂ to actually being DT. This percent change is C. All we need is the atomic D-to-T-ratio, R, as obtained from room temperature mass spectroscopy. Enriched DT is not stable at room temperature, and R is the only number we can get. We have

$$\frac{\{[D_2]-C\} + \{[DT] + C\}/2}{[T_2] + \{[DT] + C\}/2} = R \quad (3)$$

and

$$C = \frac{2[D_2] + (1-R)[DT] - 2R[T_2]}{1 + R} \quad (4)$$

We have the corrected values:

$$[DT]_c = [DT] + C \quad (5)$$

$$[D_2]_c = [D_2] - C \quad (6)$$

with [T₂] remaining the same.

As an example, we consider the sample of Fig. 2. The first values for T_2 , DT and D_2 were 2.5, 88.2, and 9.3 mol%. We obtain R equal to 1.0616 so that C is 3.8. The corrected compositions are 2.5, 92.0 and 5.5%.

We note that these infrared measurements are used for only the trio T_2 -DT- D_2 . Mass spectrometer data must be used to fold in the low level HD and HT compositions.

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Table 1. The calculated multipliers needed to quantitatively compare the infrared peaks of condensed D₂-DT-T₂. The asterisks refer to the peaks used in the analytical procedure. The matrix elements are multiplied by 1 to give the S₀(0) total multiplier and by 5/3 for the S₀(1) transitions.

Transition	Center Peak Frequency		Multipliers	
	(THz)	(cm ⁻¹)	Matrix element	Total
*1. Q ₁ (0,1)T ₂ + S ₀ (0)T ₂	77.23	2576	1.0000	1.0000
*2. Q ₁ (0,1)T ₂ + S ₀ (0)DT	78.16	2607	0.9920	0.9920
*3. Q ₁ (0,1)T ₂ + S ₀ (0)D ₂	79.03	2636	0.9847	0.9847
*4. Q ₁ (0,1)T ₂ + S ₀ (1)T ₂	79.65	2657	0.9969	1.6615
5. Q ₁ (0,1)T ₂ + S ₀ (1)D ₂	82.62	2756	0.9802	1.6337
*6. Q ₁ (0)DT + S ₀ (0)T ₂	85.59	2855	0.8912	0.8912
*7. Q ₁ (0)DT + S ₀ (0)DT	86.25	2877	0.8840	0.8840
*8. Q ₁ (0)DT + S ₀ (0)D ₂	87.42	2916	0.8776	0.8876
*9. Q ₁ (0)DT + S ₀ (1)T ₂	88.05	2937	0.8884	1.4807
10. Q ₁ (0)DT + S ₀ (1)D ₂	90.96	3034	0.8736	1.4559
*11. Q ₁ (0,1)D ₂ + S ₀ (0)T ₂	93.03	3103	0.8106	0.8106
*12. Q ₁ (0,1)D ₂ + S ₀ (0)DT	93.98	3135	0.8041	0.8041
*13. Q ₁ (0,1)D ₂ + S ₀ (0)D ₂	94.85	3164	0.7982	0.7982
*14. Q ₁ (0,1)D ₂ + S ₀ (1)T ₂	95.51	3186	0.8081	1.3469
15. Q ₁ (0,1)D ₂ + S ₀ (1)D ₂	98.42	3283	0.7946	1.3244

Table 2. A comparison of molar compositions of nearly equimolar T₂-DT-D₂ mixtures measured by magnetic sector mass spectroscopy and infrared spectroscopy.

		<u>Mol%</u>		
		<u>T₂</u>	<u>DT</u>	<u>D₂</u>
Liquid, 21 K	Mass Spec	21	49	30
	Infrared	20	52	28
Solid, 18 K	Mass Spec	22	49	29
	Infrared	21	50	29
Solid, 6 K	Mass Spec	23	49	27
	Infrared	27	50	23

Fig. 1. Collision-induced infrared spectrum of liquid regular D-T 22% T₂-50% DT-28% D₂ at 20 K. The peak numbers correspond to the entries of Table I. The bars indicate the regions used for quantitative analysis.

Fig. 2. Collision-induced infrared spectrum of enriched liquid DT at 21 K. The corrected composition is: 2.5 mol% T₂-92% DT-5.5% D₂ (run #5 in reference 1). Note how the D₂ peak sits on the broader DT peak. The peak numbers refer to Table 1.