NOTE

The Far-Infrared Spectrum of Deuterium Iodide[1]

We recently described an investigation of the far-infrared (FIR) spectrum of hydrogen iodide, HI, which resulted in an accurate set of rotational and ^{127}I electric quadrupole parameters for the molecule in its $X^1\Sigma^+$ ($v = 0$) state (*1*). In this Note, we report an extension of this work to the deuterated form of the molecule, DI.

The spectrum of deuterium iodide was recorded using the third-order tunable far-infrared (TuFIR) spectrometer at the National Institute of Standards and Technology. This spectrometer has been described in detail elsewhere (*2*). Gaseous DI was generated in a 1.1-m silica discharge tube with an outside diameter of 22 mm. A wire electrode was located 6 cm from each end of the tube. Small amounts of solid iodine were placed in the bottom of the tube. Deuterium gas was slowly flowed through the tube at a pressure of 100 Pa (0.8 Torr), and a d.c. positive-column electric discharge was ignited and maintained. A liquid-nitrogen trap prevented iodine vapor from reaching the vacuum pump. The apparatus required frequent reloading with iodine during operation. To record the absorption spectrum of DI, far-infrared radiation was passed down the discharge tube and onto a liquid-helium–cooled bolometer. The FIR radiation was frequency modulated and a lock-in amplifier was used to demodulate the absorption signals and generate first-derivative spectra. A typical spectrum of DI is shown in Fig. 1. The digitally

recorded lineshapes were fitted by the method of least squares using an equation employing five adjustable parameters: the transition frequency and intensity, the Gaussian and Lorentzian linewidths, and the spectrometer baseline.

The rotational transitions we recorded for DI cover the range $J'' = 2$–10 and are listed in Table 1. These transitions display hyperfine structure arising from the ^{127}I ($I = 5/2$; 100% natural abundance) electric-quadrupole interaction. The strong $\Delta F = \Delta J = +1$ hyperfine components are severely overlapped for all but the lowest ($J = 3$–2) rotational transition we measured; above this transition, we recorded only the weaker, but well-resolved $\Delta F = 0$ hyperfine components. However, the frequencies of several $\Delta F = \pm 1$ and 0 unblended hyperfine components of the $J = 1$–0 and 2–1 rotational lines have been reported by Gordy and coworkers (*3, 4*), so we enlarged our data set to include these earlier measurements. We then fitted the combined set by the method of least squares with a parametrized Hamiltonian appropriate for a diatomic molecule in a $^1\Sigma^+$ state with quadrupole structure (*5*).[2] During each iteration, the Hamiltonian matrix for each value of F was generated and diagonalized.

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[2] The Hamiltonian matrix elements given in this source were amended in the present work by replacing the parameter eQq with the combination $[eQq + D_{eQq}J(J + 1)]$ in order to account for centrifugal distortion of the iodine electric quadrupole interaction.
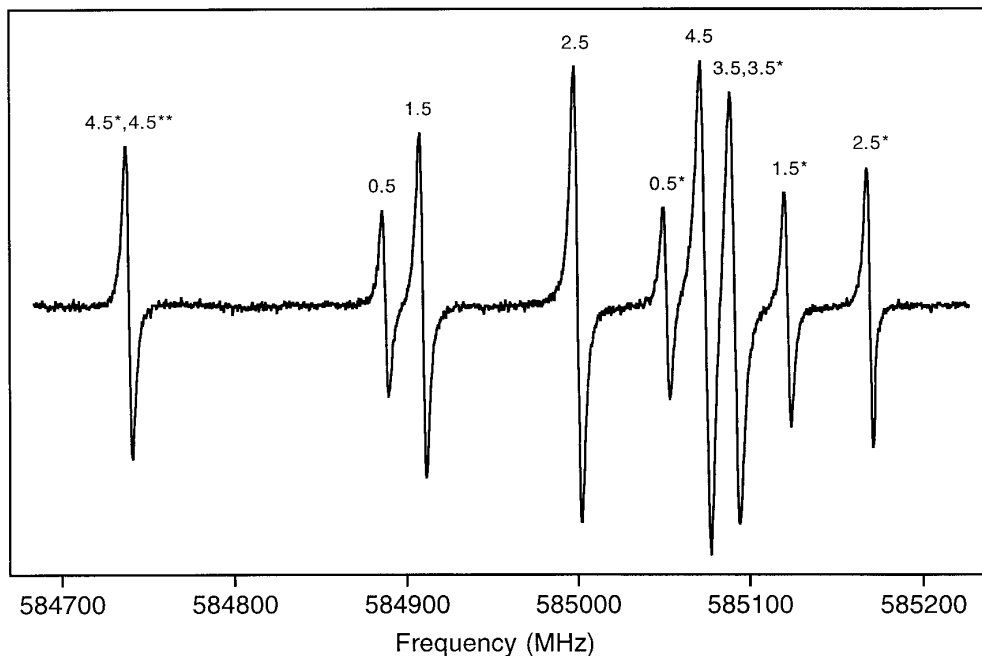

FIG. 1. The $J = 3$–2 rotational transition of DI, displaying part of the ^{127}I electric-quadrupole structure. The hyperfine components are labeled by their value of F'', with zero, one, or two asterisks to indicate the value of ΔF as +1, 0, or −1, respectively.

TABLE 1
Rotational Transitions of DI (in MHz)

J'	F'	J''	F''	Observed[a]	Calculated[b]	O − C
1	3.5	0	2.5	195 159.554 (50)	195 159.555 (11)	−0.001
1	2.5	0	2.5	194 776.100 (50)	194 776.082 (9)	0.018
1	1.5	0	2.5	195 322.706 (50)	195 322.696 (10)	0.010
2	4.5	1	3.5	390 137.417 (50)	390 137.399 (14)	0.018
2	3.5	1	3.5	389 784.989 (50)	389 784.949 (10)	0.040
2	3.5	1	2.5	390 168.462 (50)	390 168.421 (11)	0.041
2	2.5	1	2.5	390 259.212 (50)	390 259.221 (6)	−0.009
2	1.5	1	2.5	390 519.204 (50)	390 519.112 (14)	0.092
2	2.5	1	1.5	389 712.610 (50)	389 712.607 (12)	0.003
2	1.5	1	1.5	389 972.523 (50)	389 972.497 (5)	0.026
2	0.5	1	1.5	390 206.741 (50)	390 206.693 (7)	0.048
3	5.5	2	4.5	585 074.304 (18)	585 074.288 (16)	0.016
3	4.5	2	4.5	584 738.966[c]	584 738.977 (10)	
3	3.5	2	4.5	584 738.966[c]	584 738.318 (20)	
3	4.5	2	3.5	585 091.283[c]	585 091.427 (14)	
3	3.5	2	3.5	585 091.283[c]	585 090.768 (5)	
3	2.5	2	3.5	585 260.524 (34)	585 260.373 (13)	0.151
3	3.5	2	2.5	584 999.965 (12)	584 999.968 (10)	−0.003
3	2.5	2	2.5	585 169.574 (13)	585 169.573 (6)	0.001
3	1.5	2	2.5	585 381.865 (27)	585 381.868 (12)	−0.003
3	2.5	2	1.5	584 909.703 (13)	584 909.682 (8)	0.021
3	1.5	2	1.5	585 122.018 (16)	585 121.978 (5)	0.040
3	0.5	2	1.5	585 285.868 (28)	585 285.837 (9)	0.031
3	1.5	2	0.5	584 887.790 (19)	584 887.782 (7)	0.008
3	0.5	2	0.5	585 051.655 (16)	585 051.641 (5)	0.014
4	5.5	3	5.5	779 582.607 (11)	779 582.594 (9)	0.013
4	3.5	3	3.5	780 005.738[c]	780 005.765 (6)	
4	2.5	3	2.5	780 034.504 (12)	780 034.526 (6)	−0.022
4	1.5	3	1.5	780 017.234 (14)	780 017.214 (5)	0.020
5	6.5	4	6.5	974 275.034 (10)	974 275.056 (8)	−0.022
5	4.5	4	4.5	974 679.590 (11)	974 679.620 (5)	−0.030
5	3.5	4	3.5	974 741.123 (11)	974 741.138 (5)	−0.015
5	2.5	4	2.5	974 754.964 (11)	974 755.008 (5)	−0.044
6	7.5	5	7.5	1 168 778.014 (14)	1 168 777.987 (7)	0.027
6	6.5	5	6.5	1 169 019.166 (12)	1 169 019.159 (4)	0.007
6	5.5	5	5.5	1 169 166.246 (12)	1 169 166.221 (4)	0.025
6	4.5	5	4.5	1 169 245.795 (12)	1 169 245.777 (5)	0.018
6	3.5	5	3.5	1 169 280.304 (13)	1 169 280.282 (5)	0.022
7	8.5	6	8.5	1 363 053.531 (14)	1 363 053.558 (7)	−0.027
7	7.5	6	7.5	1 363 279.590 (13)	1 363 279.597 (5)	−0.007
7	6.5	6	6.5	1 363 428.564 (13)	1 363 428.586 (5)	−0.022
7	5.5	6	5.5	1 363 519.479 (12)	1 363 519.484 (5)	−0.005
7	4.5	6	4.5	1 363 568.669 (13)	1 363 568.685 (6)	−0.016
8	9.5	7	9.5	1 557 064.100 (17)	1 557 064.106 (8)	−0.006
8	8.5	7	8.5	1 557 278.905 (13)	1 557 278.890 (6)	0.015
8	7.5	7	7.5	1 557 428.506 (12)	1 557 428.502 (6)	0.004
8	6.5	7	6.5	1 557 527.177 (12)	1 557 527.156 (6)	0.021
8	5.5	7	5.5	1 557 587.370 (12)	1 557 587.373 (7)	−0.003
10	11.5	9	11.5	1 944 139.847 (11)	1 944 139.850 (10)	−0.003
10	10.5	9	10.5	1 944 339.043 (11)	1 944 339.027 (7)	0.016
10	9.5	9	9.5	1 944 488.452 (14)	1 944 488.458 (6)	−0.006
10	8.5	9	8.5	1 944 597.004 (14)	1 944 597.002 (8)	0.002
10	7.5	9	7.5	1 944 672.664 (12)	1 944 672.663 (10)	0.001
11	12.5	10	12.5	2 137 130.054 (17)	2 137 130.057 (13)	−0.003
11	11.5	10	11.5	2 137 323.615 (14)	2 137 323.613 (11)	0.002
11	10.5	10	10.5	2 137 472.682 (18)	2 137 472.705 (10)	−0.023
11	9.5	10	9.5	2 137 584.593 (17)	2 137 584.591 (12)	0.002
11	8.5	10	8.5	2 137 665.882 (26)	2 137 665.888 (16)	−0.006

[a] Values in parentheses are experimental 1σ uncertainties used in weighting each datum. The $J = 1–0$ and $2–1$ data are taken from Refs. (*3, 4*).

[b] Values in parentheses are calculated 1σ uncertainties derived from the least-squares fit.

[c] Blended line not included in the least-squares fit.

These matrices explicitly contained the $\Delta F = 0$, $\Delta J = \pm 2$ electric–quadrupole matrix elements which cause nonnegligible shifts of the energy levels. In previous work on the far-infrared spectrum of HI (*1*), the effects of these off-diagonal matrix elements were treated indirectly using perturbation theory.

Each datum in the fit was weighted by the square of the inverse of its experimental uncertainty. For our far-infrared transitions, the experimental uncertainty is the quadrature sum of the uncertainty in the FIR frequency [taken to be 10 kHz, see Ref. (*2*)] and the standard deviation of the transition frequency derived from the lineshape fitting. This combined uncertainty is typically about 12 kHz (see Table 1). Unfortunately, no experimental uncertainties were reported in the original submillimeter-wave measurements by Gordy *et al.* (*3, 4*). Judging from

the observed linewidth and signal-to-noise ratio of the spectrum displayed in Ref. (*4*), we initially estimated the uncertainty of the submillimeter-wave data to be ± 200 kHz. However, the least-squares fit showed that this estimate is too pessimistic, so the uncertainty of each transition from Refs. (*3, 4*) was set at ± 50 kHz in the final fit. This uncertainty was chosen so that the variance of the fit relative to the experimental uncertainties is roughly equivalent for the submillimeter-wave and far-infrared subsets of data; the variance of the combined fit is 2.25.

The results of the least-squares fitting are displayed in Table 2. The values for the parameters B, D, eQq, and C_I obtained in the present work agree at the 1σ level with those reported in the submillimeter-wave work (*3, 4*), but are considerably more accurate. We have also been able to obtain

TABLE 2
Rotational and ^{127}I Hyperfine Parameters
for DI (in MHz)

Parameter	Value[a]
B	97537.0842 (16)
D	1.577910 (17)
H	$1.1046 (77) \times 10^{-5}$
eQq	−1823.226 (54)
D_{eQq}	−0.04336 (85)
C_I	0.1728 (31)

[a] Values in parentheses indicate 1σ uncertainties of the last digits.

accurate values for the higher-order centrifugal distortion constant H and the centrifugal distortion correction to the quadrupole interaction D_{eQq}. With the present data, the accuracy of these constants is now similar to that determined in our complementary study of the far-infrared spectrum of the abundant isotopomer HI.

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