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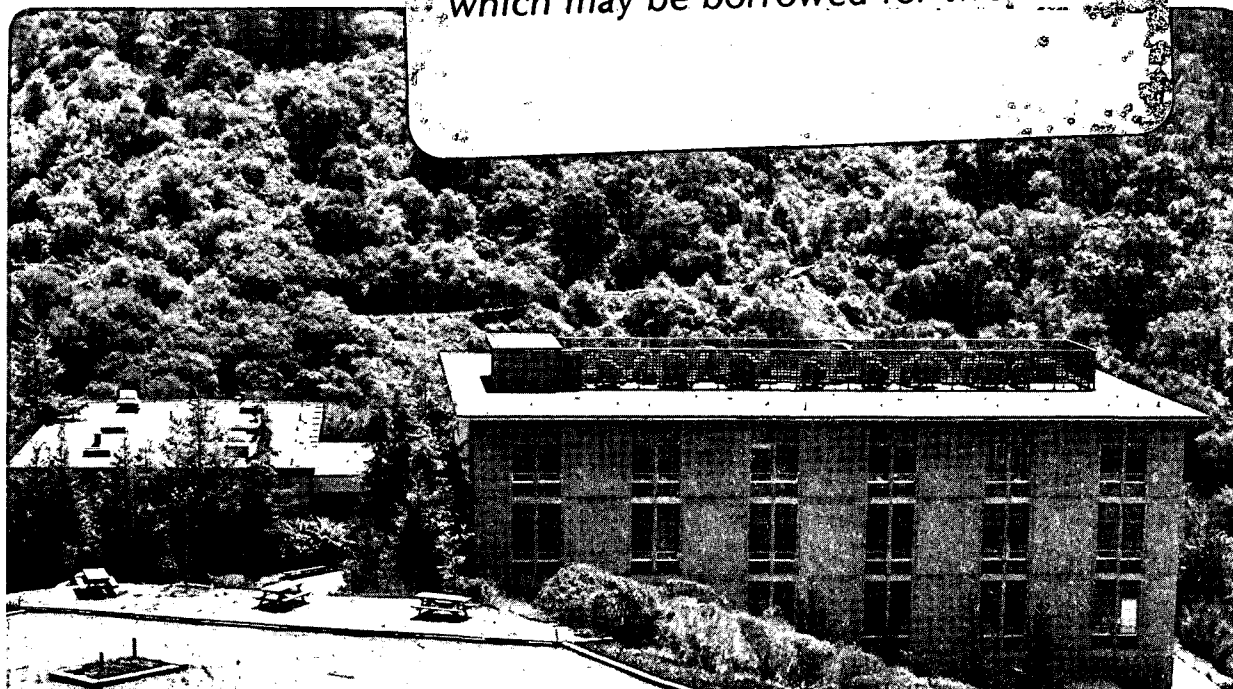
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VIBRATIONAL SPACINGS IN MOLECULAR HYDROGEN.

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Spontaneous Raman spectroscopy is used to determine line positions of the six isotopomers of molecular hydrogen: H₂, HD, HT, D₂, and T₂. State population number densities as low as $1.3 \times 10^8 \text{ cm}^{-3}$ are detected with the present experimental apparatus. This sensitivity makes possible measurements of the first overtone Q-branch line positions for H₂ and D₂. The observed line positions are given in Table I.

TABLE I. OBSERVED Q-BRANCH LINE POSITIONS (cm⁻¹)^a

J	H ₂		HD	HT	D ₂		DT	T ₂
	Q ₁	Q ₂			Q ₁	Q ₂		
0	4161.200	8087.030	3632.2 ^b	3434.9 ^b	2993.6 ^b	5868.1 ^b		
1	4155.281	8075.283	3628.4	3631.6	2991.5	5863.9		
2	4143.493	8051.964	3620.6	3425.1	2987.2	5855.6	2738.4 ^b	2461.0 ^b
3	4125.903	8017.168	3609.2	3415.6	2981.0	5843.0	2733.7	2457.5
4	4102.592			3402.8	2972.5	5826.3	2727.2	2453.0
5	4073.698		3574.9		2962.2		2719.2	2447.3
6	4039.451				2949.7		2709.8	2440.5
7					2935.2		2698.5	2432.5
8					2918.8		2686.3	2423.5
9					2900.6			2413.2
10								2402.2

^a estimated uncertainty $\pm 0.030 \text{ cm}^{-1}$ ^b estimated uncertainty $\pm 0.1 \text{ cm}^{-1}$

These observations, which include all six isotopomers and a significant number of new transitions, allow one to look for significant trends when comparing experiment with theoretical calculations. Adiabatic ab initio energy levels for molecular hydrogen are constructed from the Born-Oppenheimer potential with adiabatic, relativistic, and radiative corrections. Theoretical ab initio energy levels for all six molecular isotopomers of hydrogen are given in the recent work of Hunt, Poll, Wolniewicz⁽¹⁾. The differences, averaged over the J-levels observed, between the measured line positions and those calculated from the theoretical energy levels and our experimental measurements are presented in the left half of Table II. The differences: 1) are larger than the experimental uncertainty; 2) show an inverse dependence upon the reduced mass and 3) increase approximately linearly with vibrational quantum number. The adiabatic ab initio energy levels are obviously unable to reproduce the experimental measurements.

Nonadiabatic corrections to the energy arise because the electrons do not respond instantaneously to the positions of the moving nuclei, and therefore depend upon the reduced mass. Wolniewicz⁽²⁾ has reported nonadiabatic correction for H₂, HD, and D₂. Schwartz and LeRoy have extrapolated Wolniewicz's values to the tritium containing molecules.⁽³⁾ The average of the differences between line positions corrected for nonadiabaticity and these measurements are presented in the right half of Table II. For the low-lying vibrational energy levels ($v = 1,2$) the nonadiabatic ab initio calculations are in agreement with the present experimental measurements for all isotopomers of molecular hydrogen.

TABLE II. J-AVERAGED DIFFERENCES IN Q-BRANCH LINE POSITIONS BETWEEN EXPERIMENT AND CALCULATED FROM AB INITIO ENERGY LEVELS (cm⁻¹)

	ADIABATIC		NONADIABATIC	
	Q ₁	Q ₂	Q ₁	Q ₂
H ₂	0.854 ± 0.020	1.677 ± 0.022	0.005 ± 0.027	-0.024 ± 0.023
HD	0.63 ± 0.06	-----	0.03 ± 0.06	-----
HT	0.56 ± 0.08	-----	0.00 ± 0.10	-----
D ₂	0.37 ± 0.05	0.71 ± 0.07	0.09 ± 0.09	0.06 ± 0.09
DT	0.32 ± 0.10	-----	0.04 ± 0.08	-----
T ₂	0.16 ± 0.07	-----	-0.01 ± 0.08	-----

- The standard deviations of the differences are tabulated, not the experimental uncertainty.

References

- 1) J.L. Hunt, J.D. Poll, and L. Wolniewicz, *Can. J. Phys.* **6**, 1719 (1984).
- 2) L. Wolniewicz, *J. Chem. Phys.* **78**, 6173 (1983).
- 3) C. Schwartz and R.J. LeRoy, private communication.

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