

Rotation-Vibration Spectrum of the HD Molecule

As is well known, the hydrogen molecule (H_2) has no ordinary dipole infra-red spectrum. Its quadrupole rotation-vibration spectrum is exceedingly weak, and has only recently been found¹. In the case of HD, on account of the asymmetry, there is no longer a distinction between symmetric and antisymmetric rotational levels, and a dipole rotation-vibration spectrum can occur at least in principle. However, the change of dipole moment associated with the vibration of HD is obviously very small. The main contribution to this change is due to the fact that the electrons lag slightly behind the nuclei during the vibrational motion. Wick² has calculated according to wave mechanics the intensity of the fundamental of HD. From his data it can be estimated that the minimum absorbing path required for an observation of the fundamental of HD is 30 m. atm. For the overtones, correspondingly longer path-lengths would be required.

With the technique of long optical paths recently developed³, it appeared promising to attempt an observation of the HD spectrum in the photographic infra-red. A glass absorption tube 5 metres long was filled with HD of 1 atm. pressure. Using approximately 140 and 200 traversals, that is, absorbing paths of 700 and 1,000 metres, seven and six lines respectively were found of the 3-0 and 4-0 bands of HD (second and third overtone) near 9650 and 7400 Å. The accompanying table lists the observed wave-numbers. Even with the long path used, the intensities of the HD lines are quite low. The over-all intensity of the 4-0 band of HD is lower than that of the 3-0 band by a factor of only 3 or 4. This is noteworthy, since for ordinary dipole vibration spectra the intensity ratio of the second and third overtone is of the order 30 or 40 (for example, for hydrogen chloride).

HD ABSORPTION LINES

Designation	ν_{vac} (observed)	$o-c_1$	$o-c_2$	
3-0	R(0)	10445.536	+ 5.325	-0.004
	R(1)	10511.438	+ 5.771	-0.009
	R(2)	10565.048	+ 6.474	+0.008
	R(3)	10605.764	+ 7.403	+0.010
	P(1)	10278.419	+ 5.091	-0.015
	P(2)	10178.467	+ 5.340	+0.015
4-0	P(3)	10068.351	+ 5.748	-0.009
	R(0)	13551.127	+ 7.118	+0.008
	R(1)	13609.745	+ 8.203	+0.006
	R(2)	13652.293	+ 9.813	-0.012
	R(3)	13678.435	+11.986	-0.003
	P(1)	13387.695	+ 6.575	+0.007
P(2)	13284.020	+ 7.095	-0.012	

The best available rotational and vibrational constants of HD in the $^1\Sigma^+$ ground-state are those calculated from the constants of H_2 by Jeppesen⁴ and Urey and Teal⁵. The constants obtained directly from the ultra-violet HD spectrum are less accurate (see Jeppesen⁴). Using Urey and Teal's constants, the positions of the HD lines can be predicted. Column 3 of the table gives the differences between these predicted and the observed wave-numbers. It is seen that there is a systematic difference, principally due to the fact that the original H_2 constants from which the HD constants were calculated need revision¹. The following rotational and vibrational constants of HD were derived directly from the observed wave-numbers combined with the Raman data of Teal and MacWood⁶:

$$B_v = 45.638_5 - 1.9503(v + \frac{1}{2}) + 0.0140_0(v + \frac{1}{2})^2.$$

$$D_v = 0.02590 - 0.00084(v + \frac{1}{2}) + 0.00004_4(v + \frac{1}{2})^2.$$

$$G(v) = 3809.7_{45}(v + \frac{1}{2}) - 89.7668(v + \frac{1}{2})^2 + 0.36567(v + \frac{1}{2})^3.$$

A value $H_v = 0.0000219 \text{ cm.}^{-1}$ was assumed. The differences between the observed wave-numbers and those calculated from the new constants are given in the last column of the table.

If a sufficient amount of hydrogen and deuterium were present in the atmospheres of the major planets, the 4-0 band of HD might be used for their detection⁷. However, this would require the highest possible resolution, because of the small width of these lines.

It is hoped to observe the fundamental and first overtone of HD in the near future with the aid of a new high-dispersion infra-red spectrometer which is being built in this laboratory.

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¹ Herzberg, G., *Nature*, **163**, 170 (1949); *Can. J. Res.*, A, **28**, 144 (1950).

² Wick, G. C., *Atti Reale Accad. Lincei*, **21**, 708 (1935).

³ White, J. U., *J. Opt. Soc. Amer.*, **32**, 285 (1942). Bernstein, H. J., and Herzberg, G., *J. Chem. Phys.*, **18**, 30 (1948).

⁴ Jeppesen, C. R., *Phys. Rev.*, **45**, 480 (1934).

⁵ Urey, H. C., and Teal, G. K., *Rev. Mod. Phys.*, **7**, 34 (1935).

⁶ Teal, G. K., and MacWood, G. E., *J. Chem. Phys.*, **3**, 760 (1950).

⁷ See Herzberg, G., *Astrophys. J.*, **87**, 428 (1938).

A New Type of X-Ray Scattering

INSULATORS are characterized by discrete allowed and forbidden zones having sufficient energy width. In diamond, theoretical calculation by Kimball¹ shows that the forbidden zone width is about 7 eV., which has been experimentally verified by the appearance of the ultra-violet absorption band² at 1700 Å., that is, 7 eV. I have determined the forbidden zone widths in the case of the insulators aluminium oxide and silica from their soft X-ray absorption and valence emission spectra³. Skinner⁴ has investigated beryllium, carbon and boron in the conducting state, as well as in the insulators beryllium oxide (BeO), diamond and boron trioxide⁵. Siegbahn⁶ has investigated K_α of diamond, as well as that of graphite, the conducting variety. E. Guinner and H. Kiessig⁷ have investigated K_α , that is, K valence band spectra of boron in the pure element, in various binary alloys and in boron trioxide, which is a typical insulator. I have investigated K valence band spectra of the insulators aluminium oxide and silica.

In all the elements beryllium, boron, carbon (graphite), silicon and aluminium and in all their conducting alloys, the long wave-length K valence band satellite is absent. But in typical insulators involving these elements, there appears a long wave-length satellite which is most prominent in the case of beryllium oxide, boron trioxide and diamond, for which the characteristic X-ray wave-lengths concerned are only the K_α -radiation of metal and of oxygen. The energy gap between the peak of the long wave-length satellite and the main K_α -band for these insulators agrees well with the energy difference between the peak of the valence emission band and the approximate centre of the first allowed vacant band obtained from the absorption data.

The explanation is as follows: K_α of beryllium, boron and carbon produced by electron impact