

Oscillator Frequency and Vibrational Quanta in the Hydrogen Molecule*

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Theoretical values of the oscillator frequency and vibrational quanta in the electronic ground state of H_2 are obtained and compared with the corresponding experimental data. Agreement between the two sets of values is found to be of the order of 1 part in 10^3 . This is somewhat larger than the estimate (2 parts in 10^4) of the experimental error.

THE oscillator frequency ω_e in the electronic ground state of H_2 has been determined experimentally by Stoicheff,¹ and Herzberg and Howe,² using the relation

$$T_{v+1,0} - T_{v,0} = \omega_e - \omega_e x_e(v + \frac{1}{2}) + \omega_e y_e(v + \frac{1}{2})^2 - \dots, \quad (1)$$

where v is the vibrational quantum number, $T_{v+1,0} - T_{v,0}$ are the measured vibrational quanta, and x_e and y_e are small constants arising from the anharmonicity of the internuclear potential. The present authors have obtained theoretical values of the vibrational quanta which may be compared directly with the experimental data. The vibrational-rotational energies $T_{v,J}$ were determined by solving by an accurate numerical procedure³ the radial Schrödinger equation with the potential (in atomic units)

$$V(r) = E(r) + 1/r + J(J+1)/2\mu r^2, \quad (2)$$

TABLE I. Vibrational quanta $T_{v+1,0} - T_{v,0}$ in the electronic ground state of H_2 (in wave numbers).

v	Experimental	Theoretical
0	4161 ^a	4166
1	3926	3930
2	3695	3702
3	3468 ^b	3477
4	3242	3253

^a Stoicheff values (see reference 1).

^b Herzberg and Howe values (see reference 2).

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¹ B. P. Stoicheff, Can. J. Phys. **35**, 730 (1957).

² G. Herzberg and L. L. Howe, Can. J. Phys. **37**, 635 (1959).

³ J. W. Cooley, Math. of Comp. (to be published). See also J. P. Auffray and J. W. Cooley, Phys. Rev. **122**, 1203 (1961).

where r is the internuclear distance, $E(r)$ is the electronic energy,⁴ J is the rotational quantum number, and μ is the reduced nuclear mass.

The vibrational quanta so obtained, converted to wave numbers⁵ and corrected for the effects of interactions between the electronic and nuclear motions,⁶ are given in Table I for $v=0$ to 4, along with the corresponding experimental data for comparison. The agreement between the two sets of values is seen to be of the order of 1 part in 10^3 for v small. From the form of Eq. (1) this suggests that the experimental and theoretical ω_e must also agree within about 1 part in 10^3 . This discrepancy is somewhat larger than Herzberg's estimate (2 parts in 10^4) of the uncertainty in the experimental value and is probably due, in part, to small errors in the curvature of the theoretical potential (2), as well as to an underestimation of the effects of interactions between the electronic and nuclear motions⁷ and the neglect of relativistic effects.

It should be noted that in the present treatment no corrections for the anharmonicity of the internuclear potential were required.⁸

⁴ The best available theoretical $E(r)$, [W. Kolos and C. C. J. Roothaan, Revs. Modern Phys. **32**, 205 (1960)], was used in this calculation.

⁵ Using 1 a.u. = 219 474.62 cm^{-1} .

⁶ The correction was made by multiplying the theoretical values by the factor $1+\delta=0.99929$ [see J. H. Van Vleck, J. Chem. Phys. **4**, 327 (1936)]. This correction really applies to ω_e but $T_{v+1,0} - T_{v,0} \approx \omega_e$ for v small [see Eq. (1)].

⁷ See reference 6.

⁸ Such a correction would have been required however, if one had wanted to compare the experimental ω_e with the theoretical value obtained from the relation $\omega_e = (\gamma/\mu)^{1/2}$, where γ is the curvature of $V(r)$ at the equilibrium internuclear distance r_e . This correction was considered by Dunham [Phys. Rev. **41**, 721 (1932)]. See also the discussion of this point in reference 1.