Dipole Properties of Molecular Hydrogen

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lated from Eq. (14) also are close enough to indicate that these properties are additive for mixtures.

Finally, the least-squares treatment of data for ρ_u and ρ_v confirmed the conventional method of calculation of these quantities by taking the ratios $_u i_h/_u i_v$ and $_v i_h/_v i_v$.

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Dipole Properties of Molecular Hydrogen

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Experimental data on electron scattering, optical refractivity, and molecular anisotropy are used to construct a model dipole spectrum for molecular hydrogen which is consistent with oscillator-strength sum rules. The model spectrum is used to calculate the parallel and perpendicular dynamic dipole polarizabilities, the refractive index, the Verdet constant, the Rayleigh scattering cross section, the Rayleigh depolarization factor, and the molecular anisotropy as a function of frequency of the incident radiation. The tensor components of the van der Waals coefficient for a pair of interacting hydrogen molecules are also calculated.

I. INTRODUCTION

Approximate variational calculations[1] of various dipole properties of molecular hydrogen have been carried out as a function of the wavelength of the incident radiation. Because of inadequacies in the representation of the unperturbed and perturbed molecular wavefunctions, the calculations fail for wavelengths less than about 2500 Å. Experimental data on the oscillator-strength distributions of molecular hydrogen, supplemented by refractive-index data and sum rules, can be used to construct a model of the complete dipole spectrum which accurately reproduces dipole properties for wavelengths greater than about 1150 Å. The procedures have been applied successfully in earlier work on the inert gases, molecular hydrogen,[2] and molecular nitrogen,[3] though no distinction is there made between parallel and perpendicular transitions. Among the properties which may be investigated are the parallel and perpendicular dynamic dipole polarizabilities, the molecular anisotropy, the refractive index, the Verdet constant, the Rayleigh scattering cross section, and the Rayleigh depolarization factor. The model spectrum can also be used to calculate the tensor components of the van der Waals coefficient for a pair of interacting hydrogen molecules and to calculate the average excitation energy that controls the absorption of fast charged particles in hydrogen gas.

II. EXPERIMENTAL DATA ON HYDROGEN

Dipole oscillator strengths have been determined from measurements of energy loss of fast electrons at different scattering angles by Lassettre and Jones,[4] by Geiger,[5] and by Geiger and Topschowsky.[6] The more

[1] G. A. Victor, J. C. Browne, and A. Dalgarno, Proc. Phys. Soc. (London) **92**, 42 (1967).

[2] A. Dalgarno and W. D. Davison, Advan. At. Mol. Phys. **2**, 1 (1966).

[3] A. Dalgarno, T. Degges, and D. A. Williams, Proc. Phys. Soc. (London) **92**, 291 (1967).

[4] E. N. Lassettre and E. A. Jones, J. Chem. Phys. **40**, 1222 (1964).

[5] J. Geiger, Z. Physik **181**, 413 (1964).

[6] J. Geiger and N. Topschowsky, Z. Naturforsch. **21a**, 626 (1966).

recent measurements were taken with a resolution of about 0.007 eV and show vibrational structure in the Lyman and Werner band systems and in higher terms. Dipole oscillator strengths have also been derived from measurements of radiative lifetimes.[7] Refractive-index data between 1855 and 5462 Å are available,[8] and Bridge and Buckingham[9] have measured the Rayleigh depolarization factor for scattering of laser light at 6328 Å. Experimental values of wavelengths for the hydrogen molecular spectrum are listed by Dieke.[10]

III. CALCULATIONS

The parallel dipole oscillator strength from a state Φ_0 with energy E_0 to a state Φ_n with energy E_n is defined by

$$f_n{}^{||} = \tfrac{1}{3}[2(E_n - E_0)] \mid \langle 0 \mid \sum_{i=1}^{N} z_i \mid n \rangle \mid^2, \quad (1)$$

where all quantities are in atomic units and z_i is the z component of the position vector of the ith electron of the N electron system, where the coordinate system is referred to the midpoint of the nuclear axis with the z axis along the nuclear axis. The perpendicular dipole oscillator strength is defined by

$$f_m{}^{\perp} = \tfrac{1}{3}[4(E_m - E_0)] \mid \langle 0 \mid \sum_{i=1}^{N} x_i \mid m \rangle \mid^2, \quad (2)$$

where x_i is the x component in the same coordinate system.

The parallel component of the dynamic dipole polarizability tensor at a frequency ω for the state Φ_0 is given by

$$\alpha_{zz}(\omega) = \alpha_{||}(\omega) = 3\mathbf{S}_n \{f_n{}^{||}/[(E_n - E_0)^2 - \omega^2]\} \quad (3)$$

and the perpendicular component is given by

$$\alpha_{xx}(\omega) = \alpha_{\perp}(\omega) = \tfrac{3}{2}\mathbf{S}_m \{f_m{}^{\perp}/[(E_m - E_0)^2 - \omega^2]\}, \quad (4)$$

where the summations over n and m in Eqs. (3) and (4) are over all states, including the continuum, for which the respective oscillator strengths do not vanish. The refractive index is given by

$$n - 1 = 2\pi N \alpha(\omega), \quad (5)$$

where N is Avogadro's number and $\alpha(\omega)$ is the trace

$$\alpha(\omega) = \tfrac{1}{3}[2\alpha_{\perp}(\omega) + \alpha_{||}(\omega)]. \quad (6)$$

The anisotropy $\gamma(\omega)$ is defined by

$$\gamma(\omega) = \alpha_{||}(\omega) - \alpha_{\perp}(\omega). \quad (7)$$

[7] J. E. Hesser, J. Chem. Phys. **48**, 2518 (1968).
[8] J. Koch, Arkiv Math. Astron. Fysik. **8**, 20 (1912); M. Kirn, Ann. Physik **64**, 566 (1921).
[9] N. J. Bridge and A. D. Buckingham, J. Chem. Phys. **40**, 2733 (1964); Proc. Roy. Soc. (London) **A295**, 334 (1966).
[10] G. H. Dieke, J. Mol. Spectry. **2**, 494 (1958).

If we introduce the summations

$$S^{||}(k) = 3\mathbf{S}_n f_n{}^{||}(E_n - E_0)^k,$$

$$S^{\perp}(k) = \tfrac{3}{2}\mathbf{S}_m f_m{}^{\perp}(E_m - E_0)^k,$$

and

$$S(k) = \tfrac{1}{3}[2S^{\perp}(k) + S^{||}(k)], \quad (8)$$

the oscillator-strength sum rule may be written

$$S^{||}(0) = S^{\perp}(0) = S(0) = N. \quad (9)$$

We replace the actual oscillator-strength distributions in Eqs. (3) and (4) by model oscillator-strength distributions in which only a finite number of terms are retained:

$$\alpha_{||}(\omega) = \sum_{i=1}^{M||} \frac{a_i{}^{||}}{\bar{\omega}_i{}^{||2} - \omega^2},$$

$$\alpha_{\perp}(\omega) = \sum_{i=1}^{M\perp} \frac{\alpha_i{}^{\perp}}{\bar{\omega}_i{}^{\perp 2} - \omega^2}. \quad (10)$$

The experimental Franck–Condon factors[5] for the Lyman $(X^1\Sigma_g{}^+ - B^1\Sigma_u{}^+)$ band system were used to

TABLE I. Constants for the model molecular-hydrogen oscillator strengths.

$a_i{}^{||}$	$\bar{\omega}_i{}^{||}$	$a_i{}^{\perp}$	$\bar{\omega}_i{}^{\perp}$
0.0081	0.41096	0.07508	0.45173
0.0144	0.41697	0.12180	0.46223
0.0297	0.42281	0.11655	0.47213
0.0459	0.42849	0.07612	0.48142
0.0648	0.43401	0.04882	0.49014
0.0774	0.43939	0.02835	0.49829
0.0819	0.44462	0.01838	0.50581
0.0882	0.44970	0.01628	0.51272
0.0882	0.45464	0.01418	0.51904
0.0864	0.45943	0.35245	0.57621
0.0801	0.46410	0.57418	0.73544
0.0630	0.46863	0.46842	1.16207
0.0558	0.47300	0.08940	2.89711
0.0459	0.47728		
0.0369	0.48142		
0.0315	0.48539		
0.4167	0.57678		
0.4326	0.67414		
0.2491	1.07059		
0.0034	2.28982		

TABLE II. Dynamic dipole polarizibility in units of a_0^3 and refractive index of H_2.

λ (Å)	Theory				Experiment[a]			
	α	$\alpha_\perp$	$\alpha_{||}$	$(n-1)$[b]	α	$\alpha_\perp$	$\alpha_{||}$	$(n-1)$[b]
∞	5.450	4.774	6.803	1.364(−4)	5.437	...	...	1.360(−4)
6328.0	5.554	4.857	6.949	1.390(−4)	5.554	4.86	6.95	1.390(−4)
5462.3	5.591	4.886	7.001	1.399(−4)	5.582	...	...	1.396(−4)
4359.6	5.675	4.952	7.120	1.420(−4)	5.667	...	...	1.418(−4)
4079.0	5.708	4.979	7.167	1.428(−4)	5.701	...	...	1.426(−4)
4047.7	5.713	4.982	7.173	1.429(−4)	5.705	...	...	1.427(−4)
3342.4	5.845	5.087	7.361	1.462(−4)	5.840	...	...	1.461(−4)
2968.1	5.963	5.179	7.529	1.492(−4)	5.960	...	...	1.491(−4)
2753.6	6.056	5.253	7.663	1.515(−4)	6.055	...	...	1.515(−4)
2535.6	6.182	5.351	7.843	1.547(−4)	6.183	...	...	1.547(−4)
2379.1	6.299	5.443	8.012	1.576(−4)	6.303	...	...	1.577(−4)
2302.9	6.368	5.496	8.111	1.593(−4)	6.384	...	...	1.594(−4)
1990.5	6.766	5.803	8.692	1.693(−4)	6.771	...	...	1.694(−4)
1935.8	6.865	5.879	8.837	1.718(−4)	6.868	...	...	1.718(−4)
1862.7	7.017	5.995	9.062	1.756(−4)	7.017	...	...	1.755(−4)
1854.6	7.035	6.009	9.089	1.760(−4)	7.035	...	...	1.760(−4)
1700.0	7.471	6.337	9.739	1.869(−4)	...	...	...	...
1600.0	7.872	6.636	10.354	1.970(−4)	...	...	...	...
1500.0	8.431	7.045	11.204	2.109(−4)	...	...	...	...
1400.0	9.262	7.638	12.509	2.317(−4)	...	...	...	...
1300.0	10.625	8.573	14.730	2.658(−4)	...	...	...	...
1215.7	12.765	9.933	18.428	3.194(−4)	12.8	...	...	3.05(−4)

[a] The experimental numbers are derived from the following sources: $\lambda = \infty$, H. Schuler and K. L. Wolf, Z. Physik **34**, 343 (1925); $\lambda = 6328$, Ref. 9; $\lambda = 1215.7$ (Lyman α), Ref. 13 modified as described in the text; all other values, Ref. 8.

[b] The number in parenthesis is the power of ten by which the entry is to be multiplied.

construct the first 16 coefficients $a_i^{||}$. Four additional terms were added to Eq. (10), making $M_{||} = 20$. The additional values were initially taken from variational calculations[1] based on the Weinbaum wavefunction. Initial values of $a_i^\perp$ were chosen similarly from the experimental data on the Werner $(X\ ^1\Sigma_g^+ - C\ ^1\Pi_u)$ band system.[5,10] The first nine excited vibrational states were included, together with four additional terms from the variational calculations,[1] making $M_\perp = 13$. The values of the Werner- and Lyman-band-system oscillator strengths, and the initial values of $\alpha_i^\perp$, $\tilde{\omega}_i^\perp$, $a_i^{||}$, $\tilde{\omega}_i^{||}$ taken from the variational calculations, were then adjusted to best fit the refractive-index data,[8] subject to exactly reproducing the sum rule (9) and the measured anisotropy[9] at 6328 Å. The resulting model oscillator-strength distribution reproduces the dynamic polarizability values derived from the measurements of the refractive index[8] from 5462 to 1855 Å to at worst

0.2% and, at most wavelengths, to within 0.1%. Parameters for our final model spectrum are given in Table I. Electron-scattering data[5] yield a value of 0.26 ± 0.04 for f_B and of 0.31 ± 0.04 for f_C, the oscillator strengths of the Lyman and Werner bands, respectively, while our model distributions give 0.30 for f_B and 0.35 for f_C. Browne[11] computed a theoretical value of 0.35 for f_C and Ehrenson and Phillipson,[12] a theoretical value of 0.27 for f_B. The refractive index data at small wavelengths cannot be accurately reproduced by values of f_B and f_C much below 0.30 and 0.35, respectively.

Values of the dynamic dipole polarizability and refractive index for molecular hydrogen at selected wavelengths, derived from the model oscillator-strength spectrum, are compared in Table II with the experi-

[11] J. C. Browne, J. Chem. Phys. **44**, 835 (1966).
[12] S. Ehrenson and P. E. Phillipson, J. Chem. Phys. **34**, 1224 (1961).

TABLE III. The anisotropy, Rayleigh cross section and depolarization factor, and the Verdet constant (in units of microminutes/oersted·centimeter·atmosphere) for molecular hydrogen.

λ (Å)	γ (a_0^3)	ρ_{Ray}	Q_{Ray} (cm^2)	V
∞	2.029	0.0181	0	0
6328.0	2.092	0.0185	5.69(−28)	5.35
5462.3	2.115	0.0187	1.04(−27)	7.29
4359.6	2.168	0.0190	2.64(−27)	11.8
4079.0	2.188	0.0192	3.48(−27)	13.7
4047.7	2.191	0.0192	3.60(−27)	13.9
3342.4	2.274	0.0197	8.11(−27)	21.6
2968.1	2.350	0.0202	1.36(−26)	28.6
2753.6	2.410	0.0206	1.89(−26)	34.5
2535.6	2.492	0.0211	2.75(−26)	42.6
2379.1	2.569	0.0216	3.68(−26)	50.6
2302.9	2.615	0.0219	4.29(−26)	55.3
1990.5	2.889	0.0236	8.70(−26)	85.3
1935.8	2.958	0.0241	1.00(−25)	93.2
1862.7	3.067	0.0247	1.22(−25)	106.0
1854.6	3.080	0.0248	1.25(−25)	108.0
1700.0	3.401	0.0268	2.00(−25)	147.0
1600.0	3.710	0.0286	2.84(−25)	188.0
1500.0	4.159	0.0313	4.24(−25)	253.0
1400.0	4.871	0.0354	6.80(−25)	363.0
1300.0	6.158	0.0426	1.22(−24)	591.0
1215.7	8.495	0.0552	2.35(−24)	1070.0

mental data. The agreement at Lyman alpha (1215.7 Å) between the value reported by Gill and Heddle,[13] the present theoretical result, and an earlier theoretical estimate[14] of 12.8 a_0^3 is excellent. However, Gill and Heddle used a depolarization factor of 0.014 in the analysis of their data. The use of our more precise prediction of 0.055 modifies their value for $|n-1|$ from 3.20×10^{-4} to 3.05×10^{-4} and their value of the average dipole polarizability of 12.8 a_0^3 to 12.2 a_0^3.

IV. DIPOLE PROPERTIES

A. Rayleigh Scattering

If the rotational structure is not resolved, and the incident wavelength is not near a resonance wavelength, the Rayleigh scattering cross section is given by[14]

$$Q_{\text{Ray}}(\lambda) = (128\pi^5/9\lambda^4)\left[3\alpha(\omega)^2 + \tfrac{2}{3}\gamma(\omega)^2\right] \quad (11)$$

[13] P. Gill and D. W. O. Heddle, J. Opt. Soc. Am. **53**, 848 (1963).
[14] A. Dalgarno and D. A. Williams, Monthly Notices Roy. Astron. Soc. **124**, 313 (1962).

and the Rayleigh depolarization factor for unpolarized incident light is given by

$$\rho_{\text{Ray}}(\omega) = 6\gamma(\omega)^2/\left[45\alpha(\omega)^2 + 7\gamma(\omega)^2\right]. \quad (12)$$

Values of the molecular anisotropy $\gamma(\omega)$, the Rayleigh scattering cross section $Q_{\text{Ray}}(\omega)$, and the Rayleigh depolarization factor $\rho_{\text{Ray}}(\omega)$ for selected wavelengths are given in Table III. The theoretical values at Lyman alpha (1215.7 Å) are 8.459 a_0^3, 2.35×10^{-24} cm^2, and 0.0552, respectively, while the estimate of Ref. 14 gives 2.1×10^{-24} cm^2 for Q_{Ray}. At shorter wavelengths, the anisotropy $\gamma(\omega)$ increases more rapidly than the polarizability $\alpha(\omega)$, so that the depolarization factor $\rho_{\text{Ray}}(\omega)$ increases markedly above its long wavelength limit of about 0.018 to a value of 0.055 at Lyman alpha, where it significantly modifies the interpretation of measurements of photon scattering.[13]

B. Verdet Constant

The Verdet constant for molecular hydrogen is closely approximated by the Becquerel formula[15]

$$V = 1.007\times10^6\left[\lambda(dn/d\lambda)\right] \quad (13)$$

in units of microminutes/oersted·centimeter·atmosphere. Values of the Verdet constant at various wavelengths calculated from the model oscillator-strength distributions are given in Table III. Our values of 7.29 and 11.8 at 5462 and 4360 Å, respectively, agree with the measured values[15] of 7.06 and 11.4 to within the experimental error.

C. Moments of the Oscillator Strengths

The oscillator-strength moment functions $S^{\|}(k)$, $S^{\perp}(k)$, and $S(k)$, defined by Eqs. (8), provide useful

TABLE IV. Moment functions of the dipole oscillator-strength distribution for molecular hydrogen.[a]

k	$S^{\|}(k)$	$S^{\perp}(k)$	$S(k)$
+2	0.82	1.93	1.56(3.693)
+1	1.214	1.674	1.520(1.704)
0	2.000	2.000	2.000
−1	3.580(3.541)	2.913(2.826)	3.135
−2	6.803(6.786)	4.774(4.750)	5.450(5.429)
−3	13.48	8.433	10.12
−4	27.55	15.67	19.63

[a] The values in parenthesis are based on the accurate variational calculations of Kołos and Wolniewicz.[17]

[15] L. R. Ingersol and D. H. Liebenberg, J. Opt. Soc. Am. **46**, 538 (1956).

information on molecular structure, and many proper-ties of interest can be expressed in terms of them. Values of the moment functions for molecular hydrogen, calculated from the model spectrum, are given in Table IV. Values based on the accurate variational calculations of Kołos and Wolniewicz[16] are given for comparison. The values of $S^{||}(+2)$, $S^{\perp}(+2)$, and $S(+2)$ are not of high accuracy because of inadequacies at the large frequency part of the spectrum. The values of $S^{||}(0)$, $S^{\perp}(0)$, and $S(0)$ are exact, of course, because the model spectrum was constructed subject to this constraint. The relations[17]

$$S^{||}(-1) = 2\langle \Phi_0 \mid (z_1+z_2)^2 \mid \Phi_0 \rangle,$$

$$S^{\perp}(-1) = 2\langle \Phi_0 \mid (x_1+x_2)^2 \mid \Phi_0 \rangle,$$

$$S^{||}(-2) = \alpha_{||}(\omega=0),$$

$$S^{\perp}(-2) = \alpha_{\perp}(\omega=0) \quad (14)$$

give the moments in terms of expectation values of certain operators with respect to the ground-state wavefunction Φ_0. Since the values of these operators are a function of internuclear separation, integration with respect to the appropriate vibrational wavefunc-tion for the ground state and averaging over rotational states corresponding to the temperature of interest are necessary. Values of $S^{||}(-2)$, $S^{\perp}(-2)$ and $S(-2)$ determined by Kołos and Wolniewicz,[16] where vibra-tional and rotational averaging was effected, agree very well with the corresponding model spectrum values. The agreement is less good for $S^{||}(-1)$, where only vibrational averaging was done, and for $S^{\perp}(-1)$, where the operators were evaluated only at the equi-librium separation.

The important molecular parameter in the Bethe[18] theory of the stopping of high-velocity charged par-ticles in molecular hydrogen gas is defined by the sum

$$\ln I = \tfrac{1}{2}[\mathbf{S}_n f_n^{||} \ln(E_n-E_0) + \mathbf{S}_m f_m^{\perp} \ln(E_m-E_0)]. \quad (15)$$

The mean excitation energy I is found to be 18.6 eV, compared to previous theoretical estimates of 18.4 eV[19] and 19.5 eV.[20]

D. Long-Range Interaction

The long-range dispersion energy between two hydrogen molecules depends upon the orientation of
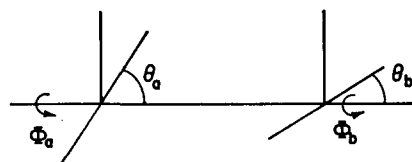

FIG. 1. Geometry for long-range H_2–H_2 interaction potential.

the molecular axes. Using the geometry shown in Fig. 1, the long-range interaction energy is[21]

$$V = -R^{-6}\{(C_{||,||}+C_{\perp,\perp}-2C_{||,\perp})$$

$$\times[\sin\theta_a \sin\theta_b \cos(\Phi_a-\Phi_b) - 2\cos\theta_a \cos\theta_b]^2$$

$$+3(C_{||,\perp}-C_{\perp,\perp})\cos^2\theta_a + 3(C_{||,\perp}-C_{\perp,\perp})\cos^2\theta_b$$

$$+(2C_{||,\perp}+4C_{\perp,\perp})\}. \quad (16)$$

According to the Casimir–Polder[22] formula, and simple geometry, the constants $C_{||,||}$, $C_{||,\perp}$, and $C_{\perp,\perp}$ can be expressed as simple linear combinations of the integrals

$$\frac{3}{\pi}\int_0^\infty \alpha_{||}(i\omega)\alpha_{||}(i\omega)d\omega,$$

$$\frac{3}{\pi}\int_0^\infty \alpha_{||}(i\omega)\alpha_{\perp}(i\omega)d\omega,$$

and

$$\frac{3}{\pi}\int_0^\infty \alpha_{\perp}(i\omega)\alpha_{\perp}(i\omega)d\omega.$$

Upon using the model spectrum, and changing the sign in the denominator of Eq. (10), trivial calculations yield values of 3.861, 1.232, and 2.426, respectively, for $C_{||,||}$, $C_{\perp,\perp}$, and $C_{||,\perp}$, with an expected accuracy of about 1%. Thus

$$V = -R^{-6}\{0.241$$

$$\times[\sin\theta_a \sin\theta_b \cos(\Phi_a-\Phi_b) - 2\cos\theta_a \cos\theta_b]^2$$

$$+3.582 \cos^2\theta_a + 3.582 \cos^2\theta_b + 9.780\}.$$

ACKNOWLEDGMENT

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[19] A. Dalgarno and D. A. Williams, Proc. Phys. Soc. (London) **85**, 685 (1965).
[20] J. D. Garcia, Phys. Rev. **147**, 66 (1966).

[21] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).
[22] H. B. G. Casimir and D. Polder, Phys. Rev. **73**, 360 (1948).