Infrared spectra of $^4HeH^+$, $^4HeD^+$, $^3HeH^+$, and $^3HeD^+$

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Isotopic species of the HeH^+ molecular ion provide an excellent testing ground for studying isotopic dependence of vibration–rotation constants because of the small masses of He and H isotopes. We have observed infrared spectra of the hot band $v = 2 \leftarrow 1$ of HeH^+ and fundamental bands of isotopic species HeD^+, $^3HeH^+$, and $^3HeD^+$, and obtained the Dunham coefficients Y_{kl}, and the isotopically independent parameters U_{kl}, Δ_{kl}^{He}, and Δ_{kl}^{H}.

I. INTRODUCTION

The HeH^+ ion has been well known to mass spectroscopists since its discovery in 1925 by Hogness and Lunn.[1] Its spectrum, however, had not been reported in any wavelength region until 1979 when Tolliver, Kyrala, and Wing[2] observed five high J P branch vibration–rotation lines of the fundamental band $v = 1 \leftarrow 0$ and a hot band $2 \leftarrow 1$ using the ingenious method of Doppler shifted ion beam laser resonance. Carrington and co-workers[3] used a similar technique to observe the spectrum of HeH^+ and its isotopes[4] near the dissociation limit. The observed transition frequencies in these studies agreed remarkably well with the theoretical predictions of Bishop and Cheung[5] and more recently of Fournier and Richard.[4] Early in 1982 Bernath and Amano[6] reported their extensive observation of the fundamental band of HeH^+ using a frequency tunable laser infrared source and accurate determination of the vibration–rotation constants of HeH^+ in the ground state and in the $v = 1$ state. Very recently Blom, Möller and Filgueira[7] reported their observation of the vibrational hot band $v = 2 \leftarrow 1$.

In the present paper we report our observation and analysis of the infrared transitions of the hot band $v = 2 \leftarrow 1$ of HeH^+ and those of the fundamental bands $v = 1 \leftarrow 0$ of isotopic species $^3HeH^+$, $^4HeD^+$, and $^3HeD^+$. Since the HeH^+ ion and its isotopes are among the simplest and lightest molecular species, they provide potentially a very useful system for checking theory, in particular the effect of the breakdown of the Born–Oppenheimer approximation.[8]

II. EXPERIMENTAL

We have used the difference frequency laser system developed by Pine[9] as the frequency tunable infrared source and the ion velocity modulation technique developed by Gudeman *et al.*[10] as the detection method. While the latter method was not required in order to discriminate ion lines from the neutral lines in this case, we nevertheless found it useful because we could use a relatively small discharge cell which can be operated under a sealed off condition to conserve the expensive ^3He isotope and still maintain high sensitivity.

The ac discharge cell was 120 cm × 1.2 cm i.d. and the ac discharge was operated at 5 kHz with a square wave voltage of ~3 kV pp and current density of ~130 mA/cm^2 r.m.s. Higher current density was found not to increase the signal. A gas mixture of He:H_2 (D_2) ~100:1 at the total pressure of ~2 Torr was used. The discharge cell was air cooled in order to observe high J transitions and the hot band.

The difference frequency laser system[9] used $LiNbO_3$ as the mixing element of the Ar and dye laser radiations. With these radiations at ~100 mW power levels, $\gtrsim 1\ \mu$W of tunable infrared radiation can be obtained in the region 2.2 ~ 4.2 μm. We have extended the region of coverage down to at least 4.4 μm by using 476.5 and 501.7 nm lines of the mixing Ar laser. The infrared radiation was passed through the discharge cell twice unidirectionally in order to increase the absorption path length. We used spectra of various reference gases such as N_2O,[11] C_2H_4,[12] H_2O,[13] H_2CO,[12] D_2O,[13] PH_3,[14] and CO_2[15] for frequency measurements. The absolute accuracy of the measured frequencies is $\sim \pm 0.002$ cm^{-1} for stronger lines when accurately known reference gas lines are available. In the worst case the uncertainty of measurement is 0.005 cm^{-1}.

III. ANALYSIS OF MEASURED FREQUENCIES

Observed frequencies of HeH^+ and isotopic species are listed in Table I. These frequencies agree remarkably well with those calculated on the basis of the *ab initio* term values of Bishop and Cheung[5] for HeH^+ and Fournier and Richard[4] for the other isotopes. In each case, the theoretical band origin is high by a few tenths of a wave number, but the deviations $\nu_{obs} - \nu_{theory}$ are remarkably constant for all low J transitions of each isotope. The variation is always less than 0.05 cm^{-1} for $0 \leqslant J \leqslant 5$. This high accuracy derives from the fact that Bishop and Cheung have improved upon the Born–Oppenheimer potential calculated by Kolos and Peek[16] and calculated adiabatic corrections to the improved potential function. Nonadiabatic, relativistic and radiative corrections have not been included, but these are expected to be smaller.

Each vibration–rotation band was fitted separately by a least squares routine using the usual power series expression for vibration–rotation term values of $^1\Sigma$ molecules

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TABLE I. Observed transition frequencies for HeH^+ isotopic species.[a]

	$^4HeH^+$ $v=1\leftarrow0$		$^4HeH^+$ $v=2\leftarrow1$		$^3HeH^+$ $v=1\leftarrow0$		$^4HeD^+$ $v=1\leftarrow0$		$^3HeD^+$ $v=1\leftarrow0$
$R(7)$	3221.752(−1)	$R(8)$	2869.478(−1)	$R(7)$	3316.761(3)	$R(10)$	2562.812(−1)	$R(4)$	2601.007(1)
$R(6)$	3207.909(−1)	$R(7)$	2869.69[d]	$R(6)$	3304.247(2)	$R(9)$	2556.772(3)	$R(3)$	2572.388(1)
$R(5)$	3186.337(−1)	$R(6)$	2861.786[d]	$R(5)$	3283.156(1)	$R(8)$	2547.048(2)	$R(2)$	2540.161(−1)
$R(4)$	3157.297(1)[b]	$R(5)$	2846.009(1)	$R(4)$	3253.785(−3)	$R(7)$	2533.732(1)	$R(1)$	2504.487(0)
$R(3)$	3121.077(0)[b]	$R(4)$	2822.683(1)	$R(3)$	3216.468(−1)	$R(6)$	2516.917(0)	$P(1)$	2378.374(4)
$R(2)$	3077.992(0)[b]	$R(3)$	2792.110(−2)	$R(2)$	3171.549(−1)	$R(5)$	2496.703(−2)	$P(3)$	2280.081(−4)
$R(1)$	3028.375(1)[b]	$R(2)$	2754.624(−1)	$R(1)$	3119.405(−1)	$R(4)$	2473.202(0)		
$R(0)$	2972.573(−1)[b]	$R(1)$	2710.563(−1)	$R(0)$	3060.433(0)	$R(3)$	2446.518(−2)		
$P(1)$	2843.904(−2)[b]	$P(1)$	2542.534(3)	$P(1)$	2923.680(−2)	$R(2)$	2416.780(0)		
$P(2)$	2771.806(0)[b]	$P(2)$	2475.815(0)	$P(2)$	2846.775(1)	$R(1)$	2384.108(1)		
$P(3)$	2695.050(0)[b]	$P(9)$	1896.992(−1)[c]	$P(3)$	2764.768(−1)	$R(0)$	2348.628(−3)		
$P(4)$	2614.030(0)[b]	$P(10)$	1802.349(1)[c]	$P(4)$	2678.113(1)	$P(1)$	2269.812(2)		
$P(5)$	2529.134(−1)	$P(11)$	1705.543(0)[c]	$P(5)$	2587.243(0)	$P(3)$	2181.432(1)[e]		
$P(6)$	2440.742(0)			$P(6)$	2492.591(2)				
$P(12)$	1855.905(0)[c]								
$P(13)$	1751.971(0)[c]								

[a] All values in cm^{-1}. The numbers in parentheses are $\nu_{obs}-\nu_{calc}$ in the last digit, resulting from the simultaneous fitting of all isotope frequencies.
[b] Measured by Bernath and Amano.
[c] Measured by Wing.
[d] Not included in the fit.
[e] Measured by diode laser.

$$E_v(J)=T_v+B_vJ(J+1)-D_v[J(J+1)]^2+H_v[J(J+1)]^3+L_v[J(J+1)]^4. \quad (1)$$

The results are summarized in Table II. The *ab initio* term values[4,5] for $0\leqslant J\leqslant 15$ were also fit to determine theoretical parameters. All of the resulting rotational parameters agree to within three standard deviations or so with the parameters which were experimentally determined. The higher order parameters which were not experimentally determinable, but which nevertheless produce a non-negligible change in transition frequency have therefore been fixed to the theoretical values. This allows lower order parameters to be determined more accurately in the fitting.

In order to fit the isotopic data simultaneously and so obtain information relating to the Born–Oppenheimer approximation more precisely, Dunham's expression[17] for the vibration–rotation term values

$$E_{v,J}=\sum_{k,l}Y_{kl}(v+\tfrac{1}{2})^k[J(J+1)]^l \quad (2)$$

has been used. The Y_{kl} have been expressed in terms of isotopically invariant parameters in accordance with Watson's expression[18]

$$Y_{kl}=\mu_c^{-(k/2+l)}U_{kl}\left[1+\frac{m_e\Delta^A_{kl}}{M_A}+\frac{m_e\Delta^B_{kl}}{M_B}\right]. \quad (3)$$

The invariant parameters are U_{kl}, Δ^A_{kl} and Δ^B_{kl}, and

$$\mu_c=\frac{M_AM_B}{(M_A+M_B-Cm_e)}, \quad (4)$$

where M_A and M_B are atomic masses of nucleus A and B, respectively, and C is the charge number of the molecule ($+1$ for HeH^+). The Δ's are correction factors normally of the order of unity, which contribute only very small correc-

TABLE II. Molecular parameters of HeH^+ isotopic species.[a]

	$^4HeH^+$ $v=1\leftarrow0$	$^4HeH^+$ $v=2\leftarrow1$	$^3HeH^+$ $v=1\leftarrow0$	$^4HeD^+$ $v=1\leftarrow0$	$^3HeD^+$ $v=1\leftarrow0$
B'	30.839 85(15)	28.089 70(27)	32.728 04(21)	19.083 56(51)	21.060 73(49)
D'	$1.585\,76(41)\times10^{-2}$	$1.562\,89(82)\times10^{-2}$	$1.797\,40(83)\times10^{-2}$	$5.747(21)\times10^{-3}$	$7.026(21)\times10^{-3}$
H'	$5.503(32)\times10^{-6}$	$4.858(61)\times10^{-6}$	$6.445(97)\times10^{-6}$	1.187×10^{-6}[c]	1.677×10^{-6}[c]
L'	-3.206×10^{-9}[b]	-4.12×10^{-9}[b]	-4.17×10^{-9}[c]	-3.55×10^{-10}[c]	···
B''	33.558 55(13)	30.839 05(45)	35.720 13(27)	20.349 03(58)	22.540 26(83)
D''	$1.621\,51(74)\times10^{-2}$	$1.584\,00(49)\times10^{-2}$	$1.840\,95(144)\times10^{-2}$	$5.847(37)\times10^{-3}$	$7.145(52)\times10^{-3}$
H''	$5.913(27)\times10^{-6}$	$5.413(24)\times10^{-6}$	$7.20(21)\times10^{-6}$	1.266×10^{-6}[c]	1.807×10^{-6}[c]
L''	-2.832×10^{-9}[b]	-3.206×10^{-9}[b]	-3.67×10^{-9}[c]	-3.45×10^{-10}[c]	···
ν_0	2910.957 32(65)	2604.1469(18)	2995.048 68(90)	2310.4859(14)	2423.4262(18)
σ[d]	0.0013	0.0021	0.0013	0.0019	0.0017

[a] All values are in cm^{-1}. Parenthetical numbers are uncertainties (1σ) in the units of the last significant figure quoted.
[b] Fixed value obtained from the *ab initio* term values of Bishop and Cheung (1979).
[c] Fixed value obtained from the *ab initio* term values of Fournier and Richard (Carrington *et al.*, 1983).
[d] Standard deviation of the fitting.

TABLE III.[a] HeH^+ isotopically invariant parameters.[a]

$U_{10} = 2889.021(111)^b\ cm^{-1}\ (amu)^{1/2}$	$U_{03} = 3.145(17)\times10^{-6}\ cm^{-1}(amu)^3$
$U_{20} = -124.305(76)^b\ cm^{-1}\ amu$	$U_{13} = -1.69(10)\times10^{-7}\ cm^{-1}\ (amu)^{7/2}$
$U_{30} = 0.156(15)^b\ cm^{-1}\ (amu)^{3/2}$	$U_{23} = -2.92(43)\times10^{-8}\ cm^{-1}\ (amu)^4$
$U_{01} = 28.114\,97(40)\ cm^{-1}\ amu$	$U_{04} = -1.061(47)\times10^{-9}\ cm^{-1}\ (amu)^4$
$U_{11} = -1.965\,99(45)\ cm^{-1}\ (amu)^{3/2}$	$\Delta_{10}^{He} = 1.040(12)^b$
$U_{21} = 5.06(31)\times10^{-3}\ cm^{-1}\ (amu)^2$	$\Delta_{10}^{H} = -0.591(17)^b$
$U_{31} = -2.405(62)\times10^{-3}\ cm^{-1}\ (amu)^{5/2}$	$\Delta_{01}^{He} = 0.878(35)$
$U_{02} = -1.066\,29(22)\times10^{-2}\ cm^{-1}\ (amu)^2$	$\Delta_{01}^{H} = -0.200(22)$
$U_{12} = 2.998(23)\times10^{-4}\ cm^{-1}\ (amu)^{5/2}$	
$U_{22} = -3.94(10)\times10^{-5}\ cm^{-1}\ (amu)^3$	

Parameters calculated from exact relations[c]

Fit I[d]	Fit II[e]
U_{02} $-1.065\,05(13)\times10^{-2}\ cm^{-1}\ (amu)^2$	$-1.065\,63(7)\times10^{-2}\ cm^{-1}\ (amu)^2$
U_{12} $2.810(30)\times10^{-4}\ cm^{-1}\ (amu)^{5/2}$	$3.029(10)\times10^{-4}\ cm^{-1}\ (amu)^{5/2}$
U_{03} $3.237(2)\times10^{-6}\ cm^{-1}\ (amu)^3$	$3.242(1.4)\times10^{-6}\ cm^{-1}\ (amu)^3$
U_{04} $-1.526(.5)\times10^{-9}\ cm^{-1}\ (amu)^4$	$-1.503(.4)\times10^{-9}\ cm^{-1}\ (amu)^4$

Derived parameters

$a_0 = 7.4217(7)^a\times10^4\ cm^{-1}$	$a_4 = 3.61(19)$
$a_1 = -2.197\,58(35)$	$a_5 = -1.6(19)$
$a_2 = 3.1045(27)$	
$a_3 = -3.673(20)$	$D_e = 16\,440(22)\ cm^{-1}$

[a] Numbers in parentheses denote one standard deviation in the last digit.
[b] Value can easily be incorrect by more than 3σ (see the text).
[c] See Eqs. (9)–(12).
[d] The results of fit I are given above under "isotopically invariant parameters."
[e] Fit II refers to a fitting of the band origins with U_{30} excluded (see the text).

tions since they are multiplied by electron mass/atomic mass. These corrections are due, in part, to the breakdown of the Born–Oppenheimer approximation.

Following Tiemann,[19] this equation is rewritten in the linearized form

$$Y_{kl} = \mu_c^{-(k/2+l)}\left[U_{kl}^e + U_{kl}^{He}\times\left(1-\frac{M_{He}^0}{M_{He}}\right) + U_{kl}^{H}\left(1-\frac{M_H^0}{M_H}\right)\right], \quad (5)$$

where M_{He}^0 and M_H^0 are atomic masses of ^4He and ^1H, respectively, in the reference molecule $^4HeH^+$. The U_{kl}^e, U_{kl}^{He}, and U_{kl}^H are related to Δ_{kl}^{He} and Δ_{kl}^H by

$$U_{kl} = U_{kl}^e + U_{kl}^{He} + U_{kl}^H \quad (6)$$

and

$$\Delta_{kl}^{He,H} = -\frac{M_{He,H}^0}{m_e U_{kl}} U_{kl}^{He,H}. \quad (7)$$

Each of the transition frequencies was weighted inversely according to the square of the estimated precision, which has been taken approximately as linewidth divided by signal to noise ratio. The values of the 18 parameters determined in the least square fitting are listed in Table III.

IV. RESULTS AND DISCUSSION

The standard deviation of the fit, defined as

$$\sigma^2 = \frac{1}{n_f}\sqrt{\frac{\sum_i (y_i - y_c)_i^2}{\sigma_i^2}}, \quad (8)$$

where σ_i is the estimated precision of the ith measurement and n_f is number of transitions minus number of parameters, is equal to 0.53. This indicates that the estimated precision of measurement was conservative for most transitions. Four Δ's were required to fit the data, and all are of the order of unity as expected. The remainder have been set to zero and their effects will be taken up by other parameters to produce slight alterations in the true values. Because of the small size of the data set and the necessity of neglecting higher order parameters, the deviations in those determined should be treated with caution. Particularly for the parameters determining the band origins, there is potential for error. The five constants U_{10}, Δ_{10}^{He}, Δ_{10}^H, U_{20}, and U_{30} determine just five band origins. If one more band was involved in the fitting, values of these parameters and their standard deviations could change considerably. If the five origins are fit without U_{30}, the result is $U_{10} = 2888.237(26)$, $\Delta_{10}^{He} = 0.892(47)$,

$\Delta_{10}^{H} = -0.7626(89)$, and $U_{20} = -123.5220(34)$, where the error estimates are 1σ and the standard deviation of the fitting was 0.006 cm^{-1}. These numbers are quite different from those given in Table III, but may actually be closer to the correct values; they are more consistent with the rotational parameters, as will be seen later.

The U_{kl} with $l \geqslant 2$ can, in principle, be calculated from the values of the U_{kl} with $l = 0$ and 1.[18] These relations can be used as a check that values of higher order parameters are approximately correct or as a way of constraining the fit or fixing parameters which could not otherwise be determined. In this case we shall simply use the exact relations[17,18]

$$U_{02} = -4U_{01}^3/U_{10}^2, \tag{9}$$

$$U_{12} = (192U_{20}U_{01}^3 + U_{11}^2U_{10}^2 - 120U_{11}U_{10}U_{01}^2)/6U_{10}^3, \tag{10}$$

$$U_{03} = 8(U_{11}U_{10} + 12U_{01}^2)U_{01}^3/3U_{10}^4, \tag{11}$$

$$U_{04} = -\frac{64U_{01}^7}{U_{10}^6}\left(5 + \frac{7U_{11}U_{10}}{6U_{01}^2} - \frac{2U_{20}}{3U_{01}} + \frac{U_{11}^2U_{10}^2}{36U_{01}^4}\right), \tag{12}$$

to check whether certain sets of parameters determined in the fit are indeed internally consistent with each other. The constants calculated by this method are also listed in Table III for comparison. The calculated values have lower uncertainties than those determined in the fit, especially for the higher order parameters. In the Table, fit II refers to the fit of band origins with U_{30} excluded. When these vibrational parameters are employed for the calculation, the results are in better agreement. Each of the constants in columns I and II can be calculated from more than one combination of the U_{kl}. Each combination leads to a slightly different number, since the fit has not been constrained to satisfy exact relations between the U_{kl}. Only one combination has been used in each case. The discrepancy in U_{02} could result from neglect of Δ_{02} parameters, since the disagreement is ~ 1 part in 10^3. Due to the incompleteness of the data, the parameters determined in the fitting are effective parameters which must be treated with caution. The agreement is not unreasonable for U_{02} and U_{12}, but worsens for U_{03} and especially U_{04}. It will be interesting to see how the results compare when more extensive data is available.

The coefficients in the Dunham potential function expansion

$$V(\xi) = a_0\xi^2\left(1 + \sum_{n=1}^{\infty} a_n\xi^n\right), \tag{13}$$

have been calculated through $n = 5$ from the exact relations[17,18]:

$$\begin{aligned}
a_0 &= \frac{U_{10}^2}{4U_{01}}, \\
a_1 &= \frac{U_{11}U_{10}}{6U_{01}^2} - 1, \\
a_2 &= \frac{1}{4}\left[\frac{U_{12}U_{10}^3}{12U_{01}^4} + \frac{19}{2} + 9a_1 + \frac{9}{2}a_1^2\right], \\
a_3 &= \frac{1}{5}\left[\frac{U_{21}U_{10}^2}{6U_{01}^3} - 5 - 10a_1 + 3a_2 + 13a_1a_2 - \frac{15}{2}(a_1^2 + a_2^2)\right], \\
a_4 &= \frac{1}{10}\left[\frac{2U_{30}U_{10}}{U_{01}^2} + 35a_1a_2 + \frac{17}{2}a_2^2 - \frac{225}{4}a_1^2a_2 + \frac{705}{32}a_1^4\right], \\
a_5 &= \frac{1}{7}\left[\frac{U_{31}U_{10}^3}{20U_{01}^4} - 7 - 21a_1 + \frac{17}{2}a_2 - 14a_3 + \frac{9}{2}a_4 - \frac{225}{8}a_1 + 45a_1a_2 - \frac{105}{4}a_1a_3 + \frac{51}{2}a_1a_4\right. \\
&\quad \left. - \frac{51}{8}a_2^2 + \frac{45}{2}a_2a_3 - \frac{141}{4}a_3 + \frac{945}{16}a_1^2a_2 - \frac{435}{8}a_1^2a_3 - \frac{411}{8}a_1a_2^2 + \frac{1509}{16}a_1^3a_2 - \frac{3807}{128}(a_1^4 + a_1^5)\right].
\end{aligned} \tag{14}$$

The results are given in Table III.

The potential function coefficients can also be determined directly from a fit of the data, using Eqs. (15) of Dunham's paper[17] to express the U_{kl} in terms of U_{10}, U_{01}, and the coefficients a_n. It is necessary to include U_{23} in the fit since Dunham gives no explicit formula, and also the Δ parameters. The standard deviation of this fit is more than an order of magnitude larger, but the results for $a_0 - a_5$ are similar to those obtained from Eq. (14). We use the results from the latter approach because the usual spectroscopic constants are all that is required to obtain them, making comparison with other molecules simpler.

We have estimated the equilibrium dissociation energy of HeH^+ from the expanded Morse potential of Dunham

$$U = D[(1 - e^{-a\xi})^2 + P_4(1 - e^{-a\xi})^4 + P_5(1 - e^{-a\xi})^5 + P_6(1 - e^{-a\xi})^6 + \cdots], \tag{15}$$

where $a = -a_1$, $\xi = r - r_e$, and $D = a_0/a_1^2$. From Dunham's formulas for P_4, P_5, and P_6, we obtain 0.056 33(58), 0.017 49(50), and $-0.004\,03(70)$, respectively, where the error estimates are 1σ. The result is $D_e = 16\,440(22)$ cm^{-1},

which is only $\sim 10\ cm^{-1}$ below the accurate *ab initio* value.[5,16] By using the same method with our OD^- results,[20] we obtain $D_e = 4.75(7)$ eV, which is similarly in agreement with other estimates. Errors resulting from the truncation of Eq. (15) and the use of effective parameters are not included in the standard deviation.

The high accuracy of D_e which is obtained by this method for HeH^+ and OD^-, when considered together with other recent work[21] suggests that this method can be useful for estimating ion dissociation energies.

The coefficients a_n determine the Born–Oppenheimer potential function. In practice, the potential function for each isotope will deviate slightly from this. Information concerning the extent and nature of this deviation is contained in the Δ parameters. These parameters are composed of a Dunham correction, which can be calculated from the coefficients in the potential function expansion, and adiabatic and nonadiabatic corrections to the Born–Oppenheimer approximation. The Δ_{01} can be expressed as[22]

$$\Delta_{01}^{\mathrm{He}} = (\Delta_{01}^{\mathrm{He}})^{\mathrm{ad}} + \frac{\mu \Delta Y_{01}^{(D)}}{m_e B_e} + \frac{(\mu g_J)_{\mathrm{H}}}{m_p} \tag{16}$$

and

$$\Delta_{01}^{\mathrm{H}} = (\Delta_{01}^{\mathrm{H}})^{\mathrm{ad}} + \frac{\mu \Delta Y_{01}^{(D)}}{m_e B_e} + \frac{(\mu g_J)_{\mathrm{He}}}{m_p} \tag{17}$$

where $(\Delta_{01}^{\mathrm{He,H}})^{\mathrm{ad}}$ is a pure adiabatic correction, $\Delta Y_{01}^{(D)}$ is the Dunham correction to B_e, given by Dunham[17]

$$\Delta Y_{01}^{(D)} = \frac{B_e^3}{4\omega_e^2}(30 + 28a_1 + 21a_1^2 + 21a_1^3 - 18a_2 - 46a_1a_2 + 30a_3), \tag{18}$$

and $(\mu g_J)_{\mathrm{He,H}}$ is the isotopically independent value of μg_J referred to the specified nucleus as origin. This last term cannot be calculated since g_J has not yet been experimentally determined. The contribution of the Dunham correction term to Δ_{01} is -0.23. The values of $(\Delta_{01}^{\mathrm{He,H}})^{\mathrm{ad}}$ can be determined from the *ab initio* adiabatic potential,[4,5] $W_n(r) + W_n^{\mathrm{ad}}(r)$, by the relations[22]

$$r_e^{\mathrm{ad}} = r_e^{B0} - \frac{1}{f}\left[\frac{dW_n^{\mathrm{ad}}(r)}{dr}\right]\Bigg|_{r_e^{B0}} \tag{19}$$

and

$$r_e^{\mathrm{ad}} = r_e^{B0}\left[1 - \frac{m_e}{M_a}\frac{(\Delta_{01}^{a})^{\mathrm{ad}}}{2} - \frac{m_e}{M_b}\frac{(\Delta_{01}^{b})^{\mathrm{ad}}}{2}\right], \tag{20}$$

where $f = [d^2W_n(r)/dr^2]\,|\,r_e^{B0}$ is the harmonic force constant. The values of r_e^{ad} for the four isotopes, determined by Eq. (19) will lead to the values of $(\Delta_{01}^{\mathrm{He}})^{\mathrm{ad}}$ and $(\Delta_{01}^{\mathrm{H}})^{\mathrm{ad}}$ when they are fitted according to Eq. (20). This will allow a prediction of g_J for HeH^+. Eventually, when more experimental and theoretical work has been done, it will be possible to check the validity of Eqs. (16) and (17).

The HeH^+ quantum mechanical system is unique in character. It is very light, has wide variability of isotopic mass ratios and many isotopes, can be conveniently studied through rotational and rovibrational spectroscopy, and is so simple that *ab initio* calculations can predict many of its properties with high precision. It is a useful system, therefore, for testing fundamental theory. Experimental and theoretical studies in more detail will be very worthwhile.

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