

Non-Born–Oppenheimer calculations of the pure vibrational spectrum of HeH⁺

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(Received 6 June 2005; accepted 11 July 2005; published online 12 September 2005)

Very accurate calculations of the pure vibrational spectrum of the HeH⁺ ion are reported. The method used does not assume the Born–Oppenheimer approximation, and the motion of both the electrons and the nuclei are treated on equal footing. In such an approach the vibrational motion cannot be decoupled from the motion of electrons, and thus the pure vibrational states are calculated as the states of the system with zero total angular momentum. The wave functions of the states are expanded in terms of explicitly correlated Gaussian basis functions multiplied by even powers of the internuclear distance. The calculations yielded twelve bound states and corresponding eleven transition energies. Those are compared with the pure vibrational transition energies extracted from the experimental rovibrational spectrum. © 2005 American Institute of Physics.

[DOI: [10.1063/1.2012332](https://doi.org/10.1063/1.2012332)]

I. INTRODUCTION

In order to enhance the precision of molecular quantum-mechanical calculations of such properties as excitation energies, electron affinities, and ionization potentials, which are currently measured with the precision exceeding a few tenths or even a few hundredths of a wave number, not only the electronic component of the wave function has to be calculated with a very high precision, but also the component describing the motion of the nuclei (vibrational and rotational), and the component describing the coupling of the electronic and the nuclear motions have to be very accurately represented. Thus, the use of an approach that departs from the Born–Oppenheimer (BO) approximation is very desirable. The development of such an approach and its implementation has been carried out for several years in our laboratory.^{1–16} The centerpiece of the development has been the use of various forms of the explicitly correlated Gaussian functions that are dependent on the distances between the particles (nuclei and electrons) forming the system. Recent calculations have demonstrated that, if extended Gaussian basis sets are used, very accurate results matching quite well the experimental data can be obtained. This applies to the properties of the ground state as well as the excited states.^{10,14,16}

As will be described later in this work, our approach is

based on separating the center-of-mass motion of the system from the internal motion and on using the variational method to determine the internal bound states of the system. In separating the center-of-mass motion we define a new internal coordinate system which is centered on one of the nuclei (called the reference particle). Such a choice does not restrict the types of the molecular systems that can be calculated. In particular, it allows for the calculation of the purely vibrational spectrum of the system, i.e., the calculation of the internal states that correspond to the zero rotational energy (rotationless states). Such calculations are performed in this work for the HeH⁺ cation.

The hydrohelium cation HeH⁺ was first observed in 1925 by Hogness and Lunn in the mass spectra of ionized He containing H₂.^{17,18} Investigations of HeH⁺ are relevant to the chemistry of astronomical objects,^{19–22} since hydrogen and helium are the two most abundant elements in the universe. The first accurate vibrational calculations of HeH⁺ in the electronic ground state based on the Born–Oppenheimer potential-energy curve were reported by Wolniewicz,²³ Kolos,²⁴ Kolos and Peek,²⁵ and Bishop and Cheung.²⁶ According to the BO calculations, HeH⁺ in its singlet ground state ¹Σ⁺ has a bond distance of about 0.77 Å and a dissociation energy of 44.6 kcal/mol.²⁶ The relatively large HeH⁺ permanent dipole moment has allowed highly precise measurements of vibrational-rotational and pure rotational gas-phase spectra of this system and the determination of the transition energies.^{18,27–39} Among the first accurate experi-

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ments concerning the HeH⁺ rovibrational spectrum, one should mention the work by Tolliver *et al.*²⁸ and the works by Carrington *et al.*^{29,31} The latter group has observed vibrational-rotational lines of HeH⁺ and its isotopic species near the dissociation limits. One should also mention the first direct infrared measurement of the absorption spectra of HeH⁺ by Bernath and Amano³⁰ who measured nine transitions in the fundamental 1-0 band and determined molecular constants for the $\nu=0$ and $\nu=1$ vibrational states. Also, the work of Liu *et al.*³³ and the work by Crofton *et al.*³⁴ provided additional data on the vibration-rotation transitions for both fundamental and some hot bands. Furthermore, additional high-quality data have been more recently presented by Matsushima *et al.*³⁶ including some very precise measurements of several pure rotational transitions at low J values for all four isotopomers of HeH⁺ (⁴HeH⁺, ⁴HeD⁺, ³HeH⁺, and ³HeD⁺) and by Liu and Davies,^{18,37} who measured pure rotational high J transitions for levels up to the dissociation threshold in the $\nu=0, 1$, and 2 states of ⁴HeH⁺. The latter team also measured some vibrational-rotational transitions involving levels near dissociation for ν up to 7 as well as some pure rotational transitions involving quasibound levels.

The available data on the vibrational-rotational and on the pure rotational transition energies for the ground electronic state of ⁴HeH⁺, ⁴HeD⁺, ³HeH⁺, and ³HeD⁺ were used by Coxon and Hajigeorgiou³⁸ to generate analytical fits of the “experimental” Born–Oppenheimer potentials. Based on those potentials, they derived high-order centrifugal distortion constants as well as level widths for quasibound levels. The vibrational motion of isotopomers of HeH⁺ has been also investigated by the electron nuclear dynamics method.⁴⁰

II. METHOD USED IN THE CALCULATIONS

The total nonrelativistic Hamiltonian for HeH⁺ in the laboratory Cartesian coordinate system has the following form:

$$\hat{H}_{\text{TOT}} = - \sum_{i=1}^4 \frac{1}{2M_i} \nabla_i^2 + \sum_{i=1}^4 \sum_{j>i}^4 \frac{Q_i Q_j}{R_{ij}}, \quad (1)$$

where the masses, charges, and positions of the four particles forming HeH⁺ are denoted as M_i , Q_i , and \mathbf{R}_i , respectively (the first two are the nuclei of the He and H atoms, and the last two are the electrons). The laboratory frame Hamiltonian includes the kinetic-energy operator for each particle and the Coulombic interactions between each pair of the particles. $R_{ij} = |\mathbf{R}_j - \mathbf{R}_i|$ are interparticle distances. The Hamiltonian (1) is transformed to separate the center-of-mass Hamiltonian motion, thereby reducing the four-particle problem to a three-pseudoparticle problem described by the internal Hamiltonian \hat{H} . In this transformation the laboratory Cartesian coordinate system is replaced by a system whose first three coordinates are the laboratory coordinates of the center of mass, and the remaining nine coordinates are the Cartesian coordinates in the internal coordinate system whose origin is placed at the helium nucleus (particle 1 with mass M_1 called the reference particle). The other particles referred to the reference particle using the Cartesian position vectors \mathbf{r}_i

defined as $\mathbf{r}_i = \mathbf{R}_{i+1} - \mathbf{R}_1$. The resulting internal Hamiltonian \hat{H} is

$$\hat{H} = - \frac{1}{2} \left(\sum_i^3 \frac{1}{m_i} \nabla_i^2 + \sum_{i \neq j}^3 \frac{1}{M_1} \nabla_i \nabla_j \right) + \sum_{i=1}^3 \frac{q_0 q_i}{r_i} + \sum_{i < j}^3 \frac{q_i q_j}{r_{ij}}, \quad (2)$$

where $'$ denotes vector transposition. The Hamiltonian (2) describes a system with the charge of the reference particle placed in the origin of the coordinate system ($q_0 = Q_1$) and three pseudoparticles, or internal particles, which are characterized by the reduced masses $m_i = M_1 M_{i+1} / (M_1 + M_{i+1})$ and charges $q_i = Q_{i+1}$. The pseudoparticles are moving in the spherically symmetric potential of the reference particle. The second term in the parentheses in (2) is the mass polarization term, which couples the motion of all pseudoparticles. In the potential-energy terms r_i and r_{ij} are defined as $r_i = |\mathbf{r}_i|$ and $r_{ij} = |\mathbf{R}_{j+1} - \mathbf{R}_{i+1}| = |\mathbf{r}_j - \mathbf{r}_i|$.

In our works concerning non-BO calculations on small diatomic molecular systems^{3–6,10,12–14,16} we have shown that the explicitly correlated Gaussian basis set involving functions with preexponential multipliers consisting of the internuclear distance \mathbf{r}_1 raised to a non-negative power m_k

$$\phi_k = r_1^{m_k} \exp[-\mathbf{r}'(A_k \otimes I_3)\mathbf{r}], \quad (3)$$

is capable of very effectively describing nonadiabatic zero angular momentum states of diatomic systems with σ electrons. The above function is a one-center correlated Gaussian with exponential coefficients forming the symmetric matrix A_k . \mathbf{r} is a $3n \times 1$ vector of the internal Cartesian coordinates \mathbf{r}_i of the n pseudoparticles, and I_3 is the 3×3 identity matrix. ϕ_k are rotationally invariant functions as required by the symmetry of the internal ground-state problem described by the Hamiltonian (2). The presence of $r_1^{m_k}$ factor in (3) shifts the function peak away from the origin. This shift depends on the value of m_k and on the exponential parameters A_k . To describe a diatomic system, the maximum of the trial wave function in terms of r_1 should be around the equilibrium internuclear distance of the system. In the variational calculation the maxima of ϕ_k 's are adjusted by optimization of m_k 's and A_k 's. More details on the Hamiltonian transformation and the selection of the basis functions for diatomic calculations can be obtained by the readers from recent reviews.^{1,2}

The ground- and excited-state nonadiabatic wave functions for HeH⁺ in the present calculations were obtained by minimizing the Rayleigh quotient:

$$E(\{c_k\}, \{m_k\}, \{A_k\}) = \min \frac{c' H(\{m_k\}, \{A_k\}) c}{c' S(\{m_k\}, \{A_k\}) c}, \quad (4)$$

with respect to the expansion coefficients of the wave function in terms of the basis functions c_k , the basis-function exponential parameters $\{A_k\}$, and the preexponential powers $\{m_k\}$.

In general, simultaneous optimization of the energy functional (4) with respect to nonlinear parameters of all basis functions represents a difficult and a very time-consuming computational task when the number of basis

functions exceeds a few tenths or, in the best case, a few hundredths. To achieve the best results in the parameter optimization with the least computational effort, we have recently implemented a hybrid method that combines the gradient-based optimization (i.e., the optimization that makes use of the analytical expressions for the gradient as opposed to the finite-difference gradient evaluation) with the stochastic selection method.^{12,13} The strategy is based on alternating the gradient-based and the stochastic-based optimizations in growing the basis set from a small initial set generated in a gradient-based optimization to the final set. The basis set for each vibrational state of HeH⁺ was generated in a separate calculation. To achieve high accuracy we used 4500 basis functions for each state. We believe that with these many functions in the basis the energies were converged to seven decimal figures. The range of the preexponential powers $\{m_k\}$ used was from 0 to 250, and the powers were partially optimized for each state.

After the wave functions for all 12 ($\nu=0, \dots, 11$) states were generated, we calculated the expectation values of the interparticle distances (i.e., the internuclear distance, the distances between an electron and a nucleus, and the interelectron distance for each state, as well as the squares of the distances). The algorithm for calculating the expectation values of the distances was described in a previous work.¹⁶ In the calculations we used the following values for the nuclear masses: $m_{\text{He}}=7294.299\,536\,3m_e$ (⁴He isotopomer), $m_p=1836.152\,672\,61m_e$ taken from Ref. 41. Here, m_e stands for the mass of the electron.

III. ESTIMATION OF PURE VIBRATIONAL TRANSITIONS OF ⁴HeH⁺ FROM MW AND IR SPECTRA

The available microwave (MW) and IR spectra of the four isotopomers ⁴HeH⁺, ⁴HeD⁺, ³HeH⁺, ³HeD⁺ include 51 pure rotational transitions for $\nu=0, 1, 2$ and $J=0 \rightarrow 1$ up to $J=28 \rightarrow 29$ (Refs. 42–45) as well as the vibrational-rotational transitions for $\nu=0 \rightarrow 1$ up to $\nu=9 \rightarrow 13$ and $J=0 \rightarrow 1$ up to $J=22 \rightarrow 21$ (Refs. 42 and 46). The data on bound-quasibound and quasibound-quasibound transitions are also available.^{18,29,31,42,45}

To estimate the pure vibrational transitions of ⁴HeH⁺ from the available MW and IR spectra, we used the method called the deformational self-consistent (DS-c) procedure. It has been tested on some neutral molecules^{50,51} and then successfully applied to ArH⁺ (Refs. 52 and 53) and KrH⁺ (Ref. 54) in the ground electronic state $X^1\Sigma^+$. The DS-c method employs the Herman–Ogilvie wave equation:⁵⁵

$$\left(-B_0 \frac{d^2}{dx^2} + U_w(x) - E_w\right) \psi_w(x) = 0, \quad (5)$$

with an effective potential:⁵²

$$U_w(x) = \frac{B_0 J(J+1)[1 + \alpha(x) - \beta(x)]}{(1+x)^2} + V(x)[1 - \beta(x)] + V(x)' + E_w \beta(x), \quad (6)$$

that includes adiabatic $V(x)'$, nonadiabatic rotational $\alpha(x)$, and vibrational $\beta(x)$ corrections to the BO energy levels. Here, $B_0 = \hbar^2 / (2mR_0^2)$ denotes the rotational parameter for the

BO equilibrium internuclear separation R_0 , $x = (R - R_0) / R_0$ is the Dunham's variable,⁵⁷ and J and ν are the rotational and vibrational quantum numbers, respectively. In the calculations we used the effective reduced atomic mass:

$$m = \frac{m_{\text{He}} m_{\text{H}}}{m_{\text{He}} + m_{\text{H}} - q m_e}, \quad (7)$$

in which the parameter q represents the electron mass “shift” representing the motion of the electrons and specific to HeH⁺.⁵⁶ The above form of the reduced mass with the additional adjustable parameter q enables the reproduction of the spectral data of ⁴HeH⁺ with the normalized standard deviation of $\hat{\sigma} = 1.2056$, whereas without the adjustable parameter ($q=0$) the standard deviation of the results increases to $\hat{\sigma} = 1.2923$.

All radial functions in (6) are expanded into a series of the Ogilvie–Tipping variable $z = x / (1 + x/2)$ that remains finite $-2 \leq z < 2$ throughout the whole range of the internuclear distance ($0 \leq R < \infty$). Additionally, following the Herman–Ogilvie theory,⁵⁵ we included in (6) an ionic correction:

$$\kappa^2 Q m_e / m, \quad \kappa = n'_a / (n'_a + n'_b) - n_a / (n_a + n_b), \quad (8)$$

where $n_{a(b)}$ are nuclear masses of ⁴He and H, respectively, m_e is the mass of the electron, and Q is the net charge on the molecule. The nuclear masses and the reduced atomic mass of the isotopomer are denoted by primed quantities; to calculate κ the masses n'_a and n'_b are automatically inserted into (8) during the fitting procedure.

The radial functions in (6) for HeH⁺ have the following forms:

$$V(x) = c_0 z^2 \left(1 + \sum_{i=1} c_i z^i\right), \quad (9)$$

$$V(x)' = m_e \sum_{i=1} \sum_{\mu=\text{He,H}} u_i^\mu m_\mu^{-1} z^i, \quad (10)$$

$$\alpha(x) = m_e \sum_{i=0} \sum_{\mu=\text{He,H}} t_i^\mu m_\mu^{-1} z^i + \kappa^2 Q m_e / m, \quad (11)$$

$$\beta(x) = m_e \sum_{i=0} \sum_{\mu=\text{He,H}} s_i^\mu m_\mu^{-1} z^i + \kappa^2 Q m_e / m. \quad (12)$$

The presence of the term $\kappa^2 Q m_e / m$ in (11) and (12) ensures mass independence of the coefficients $t_i^{\text{He,H}}$ and $s_i^{\text{He,H}}$.⁵⁵

The wave equation (5) solved using the semiclassical WKB scheme⁵⁷ produces the eigenvalues:^{50,52}

$$E_w = b_0^w + \sum_{k=0} Y_{k0}(v+1/2)^k, \quad (13)$$

where Y_{k0} 's are Dunham's vibrational coefficients. The analytical expressions of Y_{k0} 's can be found in.⁵⁷ We made the following substitution: $\{R_e, a_n\} \rightarrow \{R_w, a_n^w\}$, where

$$a_0^w = b_2^w \quad a_{s>0}^w = b_{s+2}^w / a_0^w, \quad (14)$$

$$b_n^w = (n!)^{-1} [d^n U_w(R) / dR^n]_{R=R_w}, \quad (15)$$

TABLE I. Radial parameters of $\text{HeH}^+ X^1\Sigma^+$. (Values in parentheses are standard errors for the corresponding parameters in units of the least significant digit. In calculations of the pure vibrational transitions of $^4\text{HeH}^+$, we used values with additional digits specified after parentheses.)

c_0/cm^{-1}	74 209.95(2 5)15 078 3
c_1	-1.197 789 (33)0 3
c_2	0.542 34(1 3)37 7
c_3	-0.283 65(6 7)56 7
c_4	0.179 4(37) 492 1
c_5	0.088 6(43) 413 4
c_6	-0.643 (25)1 489 6
c_7	0.663 (70)8 282 6
c_8	1.227 (67)6 383 1
c_9	-3.45(2 7)22 880 8
c_{10}	4.36(5 1)87 962 4
c_{11}	-4.10(4 5)63 018 2
c_{12}	1.94(1 7)86 469 5
t_0^{He}	-0.355 (17)1 922 6
t_0^{H}	0.539 1(19) 216 8
s_0^{He}	-0.257 (48)2 128 8
s_0^{H}	0.384 7(49) 073 0
$u_1^{\text{He}}/\text{cm}^{-1}$	528 13(1 005).418 419 45
$u_1^{\text{H}}/\text{cm}^{-1}$	-3 240 3(86).311 981 58
$R_e/(10^{-10} \text{ m})$	0.774 335 53(15)
q	-0.093 (21)8 708 4
$\hat{\sigma}$	1.205 6
$F/10^{15}$	2.548 6
g_0	0.449 4(64) ^a
μ_0	1.664 (32)

^aRotational g factor g_0 and dipole moment μ_0 are calculated for $^4\text{HeH}^+$.

$$B_{wv} = \hbar^2/(2mR_{wv}^2), \quad (16)$$

where R_{wv} is calculated in an analytical form⁵⁰ using the criterion for the minimum of the effective potential (6):

$$\left[\frac{dU_{wv}(R)}{dR} \right]_{R=R_{wv}} = 0 \quad (17)$$

(here the MAPLE processor⁵⁸ was used).

The energy eigenvalues obtained from (13) were applied to evaluate the coefficients of the radial functions (9)–(12). The coefficients were directly fitted to the measured rotational and vibrational-rotational spectra using the weighted nonlinear least-square routine with weights taken as inverse squares of the uncertainties of the experimental data. In the calculations we used the vibrational Dunham's coefficients:⁵⁹

$$Y_{k0} = \sum_{h=0}^7 Y_{k0}^{2h}, \quad (18)$$

up to the 14th order for $0 \leq k \leq 8$, including a_n for the parameters of the potential in the range of $0 \leq n \leq 14$. Consequently (15) contains derivatives up to the 16th order.

To obtain the best set of parameters fitted from the spectra, we used the following criteria: the minimum number of the fitted parameters consistent with the minimum value of the normalized standard deviation $\hat{\sigma} \approx 1$, the maximum value of the F statistics, and the optimum values of the estimated standard error σ_i of each fitted parameter and of the correlation coefficient $cc(i, j)$ between the i and j parameters. The results of the calculations are presented in Table I. The val-

TABLE II. IR and MW HeH^+ data used in the combined isotopomer analysis.

	v	J_{\min}	J_{\max}	lines	Reference
$^4\text{HeH}^+$	0	0	15	8	18, 43, and 44
	1	10	14	4	18
	2	13	15	2	18
	0→1	0	14	22	34, 35, and 46–49
	1→2	0	11	21	34, 35, 46, 48, and 49
	2→3	4	8	7	35 and 49
	3→4	13	14	1	49
	4→5	10	11	1	18
$^4\text{HeD}^+$	0	0	19	5	44 and 45
	0→1	0	11	20	34 and 49
	1→2	0	0	9	35 and 49
	2→3	2	9	5	35 and 49
$^3\text{HeH}^+$	0	0	2	2	44
	0→1	0	8	14	34
	0	1	3	2	44
$^3\text{HeD}^+$	0	1	3	2	44
	0→1	0	5	5	34

ues given in parentheses are the uncertainties of the estimation of the standard deviation. Each value is given in units of the last quoted digit of the fitted parameter; the additional digits permit the calculation of the line position to within the residuals of the fit.

In the preliminary calculations we used all available spectral data for HeH^+ (Refs. 42–49), except those representing bound-quasibound and quasibound-quasibound transitions. We determined that a simple power expansion of the BO potential (9) is unable to reproduce those transitions. The spectral data were selected according to the following criterion:

$$\sigma_i = \frac{\nu_i^{\text{obs}} - \nu_i^{\text{calc}}}{a_i} < 3.0. \quad (19)$$

The criterion was previously applied by Coxon and Hajigeorgiou.⁵⁶ In the above inequality σ_i is the i th reduced residual and a_i is the estimated accuracy of the measurement. All data which have not passed this test were excluded from the fit, and thus the original set of 183 transitions was reduced to a set of 145 transitions, including 23 pure rotational and 122 rotational-vibrational lines. Among those lines there were seven duplicate lines assigned to different wave numbers. The data used in the combined isotopomer spectral analysis are presented in Table II.

The DS-c method enables the reduction of the wave numbers of the 145 pure rotational and vibrational-rotational transitions of HeH^+ in four isotopic variants to 21 free adjustable radial parameters. To test the reliability of the evaluated parameters we calculated the electric dipole moment and the rotational g factor of $^4\text{HeH}^+$ employing the following relationships:⁵²

$$\mu_0 = (eR_0/2)(t_0^{\text{He}} - t_0^{\text{H}}), \quad (20)$$

TABLE III. Expectation values of purely vibrational states of the HeH⁺ ion: the total nonadiabatic energy ($\langle H \rangle$), the internuclear distance ($\langle r_1 \rangle$), the distance between the He nucleus and an electron ($\langle r_2 \rangle$), the distance between the proton and an electron ($\langle r_{12} \rangle$), the distance between electrons ($\langle r_{23} \rangle$), and the squares of the distances. All values are in a.u.

v	$\langle H \rangle$	$\langle r_1 \rangle$	$\langle r_2 \rangle$	$\langle r_{12} \rangle$	$\langle r_{23} \rangle$	$\langle r_1^2 \rangle$	$\langle r_2^2 \rangle$	$\langle r_{12}^2 \rangle$	$\langle r_{23}^2 \rangle$
0	-2.9710784594	1.5177	0.9356	1.5619	1.4052	2.3283	1.1809	2.7775	2.4107
1	-2.9578148743	1.6339	0.9430	1.6718	1.4210	2.7472	1.2093	3.1932	2.4762
2	-2.9459492135	1.7650	0.9491	1.7981	1.4346	3.2529	1.2343	3.7006	2.5350
3	-2.9354895028	1.9164	0.9535	1.9463	1.4455	3.8798	1.2548	4.3363	2.5847
4	-2.9264582297	2.0969	0.9561	2.1254	1.4530	4.6857	1.2695	5.1607	2.6229
5	-2.9188926470	2.3209	0.9564	2.3504	1.4568	5.7748	1.2769	6.2818	2.6462
6	-2.9128422218	2.6156	0.9543	2.6483	1.4560	7.3537	1.2751	7.9108	2.6512
7	-2.9083565162	3.0354	0.9494	3.0733	1.4506	9.8894	1.2626	10.521	2.6347
8	-2.9054434203	3.7033	0.9424	3.7473	1.4410	14.633	1.2399	15.368	2.5975
9	-2.9039512769	4.9189	0.9353	4.9654	1.4307	25.609	1.2147	26.471	2.5538
10	-2.9034217662	7.4831	0.9312	7.5231	1.4246	59.329	1.1997	60.313	2.5274
11	-2.9033104419	16.040	0.9298	16.064	1.4225	283.36	1.1945	284.46	2.5182

$$g_0 = m_p \left(\frac{t_0^{\text{He}}}{m_{\text{He}}} + \frac{t_0^{\text{H}}}{m_{\text{H}}} \right). \quad (21)$$

From the relations (20) and (21) and using the parameters $t_0^{\text{He,H}}$ specified in Table I, we evaluated the BO equilibrium ($R=R_0$) values of the rotational g factor $g_0=0.4494(64)$ and the $^4\text{HeH}^+$ dipole moment $\mu_0=1.664(32)$ D at the polarity of $[\text{HeH}^+]^+$. The calculated g factor differs slightly from the calculated *ab initio* value $g_0=0.5577$ extrapolated to $J=0$,⁶⁰ whereas the calculated dipole moment acceptably conforms with the *ab initio* result of $\mu_0=1.66$ D obtained by Dabrowski and Herzberg.⁶¹

IV. RESULTS AND DISCUSSION

The energies for all twelve rotationless bound vibrational states of HeH⁺ obtained in the calculations are presented in Table III. The availability of the wave functions describing the rotationless internal motion of HeH⁺ in the ground and excited states allowed the calculation of the expectation values of the interparticle distances and their squares. The averaged interparticle distances are also shown in Table III. As expected, the average internuclear distance ($\langle r_1 \rangle$) increases with the vibrational excitation. In the ground state this distance is equal to 1.5177 a.u. and increases to 16.040 a.u. for the highest excited state. The distance between an electron and the helium nucleus ($\langle r_1 \rangle$) equals 0.9356 a.u. in the ground state first and slightly increases with the excitation level, but starting with the $v=6$ level it starts to decrease. This trend indicates that the two electrons stay close to the helium nucleus for all vibrational states. In the lowest states, where the average distance between the helium nucleus and the proton is still relatively short, the electron density polarizes somewhat towards the proton. This polarization slightly increases with the excitation level. However, starting with the $v=6$ level, the proton becomes so far removed from the helium atom that the electronic polarization starts to decrease and the electrons center around the helium nucleus as they do in an isolated helium atom. The localization of the electrons around the helium nucleus and away from the proton is also apparent in the behavior of the average electron-proton distance ($\langle r_{12} \rangle$). In the ground state this distance is equal to

1.5619 a.u., but increases to 16.0641 a.u. for the highest excited state. The latter value is almost equal to the average internuclear distance for that state. The average interelectron distance ($\langle r_{23} \rangle$) is affected to a small extent by the vibrational excitation. This indicates that the electrons do not part from each other due to the interaction with the proton, but they stay bonded to the helium nucleus. Thus, as expected, the HeH⁺ ion, regardless of the level of the vibrational excitation, can be described as a complex of a slightly polarized helium atom and a proton which, as the level of the vibrational excitation increases, becomes increasingly more distant from the helium atom.

In Table IV the 11 vibrational transitions between adjacent energy levels obtained in the calculations are compared with the previous most accurate calculations for the two lowest transitions of Bishop and Cheung.²⁶ A comparison is also made to the pure vibrational $^4\text{HeH}^+$ transitions obtained from the available experimental data according to the procedure described above. In this procedure the radial parameters from Table I were used. The comparison indicates that the first four estimated frequencies ($\nu_{0 \rightarrow 1}$, $\nu_{1 \rightarrow 2}$, $\nu_{2 \rightarrow 3}$, and $\nu_{3 \rightarrow 4}$) are in excellent agreement with the results of the calculations,

TABLE IV. The comparison of the calculated pure vibrational transition energies with the energies derived from the experimental data. All values are in cm⁻¹. The experimental transitions shown in parentheses corresponding to transitions 4→5 and higher have not been determined with the same accuracy as the four lowest transitions.

$v' \rightarrow v''$	ΔE , this work	ΔE , experiment	Previous calculations
0→1	2911.0203	2910.9590	2911.32 ^a
1→2	2604.2112	2604.1472	2604.34 ^a
2→3	2295.6411	2295.5792	
3→4	1982.1352	1982.2025	
4→5	1660.4534	(1661.2738)	
5→6	1327.9149	(1330.5780)	
6→7	984.4986	(988.2319)	
7→8	639.3506	(631.9510)	
8→9	327.4876		
9→10	116.2142		
10→11	24.4329		

^aReference 26.

TABLE V. The convergence of $0 \rightarrow 1$, $6 \rightarrow 5$, and $11 \rightarrow 10$ transition energies (in cm^{-1}).

Basis size	$0 \rightarrow 1$	$6 \rightarrow 5$	$11 \rightarrow 10$
500	2913.7468	1333.8461	...
1000	2911.3600	1326.9789	...
1500	2911.1192	1328.0129	24.0944
2000	2911.0505	1328.0193	24.2728
2500	2911.0326	1327.9666	24.3705
3000	2911.0263	1327.9334	24.4101
3500	2911.0237	1327.9453	24.4154
4000	2911.0216	1327.9206	24.4253
4500	2911.0203	1327.9149	24.4329

whereas the remaining ones differ from them more significantly. The likely reason for the discrepancy is that only a few spectral lines are available for the $4 \rightarrow 5$, $5 \rightarrow 6$, and $6 \rightarrow 7$ transitions and could be used to evaluate the parameters of the radial functions. When more experimental data that include higher vibrational transitions in the $P(J)$ and $R(J)$ branches for HeH^+ become available, the higher pure vibrational transitions will be determined with much higher accuracy.

Finally, in Table V we demonstrate how our non-BO transition frequencies converge with the increasing number of the basis functions. We show only three frequencies, as the behavior of the others has been very similar. Naturally, the transition frequencies that involve lower states are converged somewhat better since the wave functions of those states have fewer nodes and a smaller number of basis functions is normally needed to describe the wave functions of those states with the same accuracy as for the higher excited states.

V. CONCLUSIONS

Highly accurate non-Born–Oppenheimer calculations of pure vibrational transitions are reported for the HeH^+ ion. In this system the electron density is asymmetric and it is concentrated around the helium nucleus. Differences of the total energies between adjacent energy levels calculated using spherically symmetric, explicitly correlated Gaussian basis functions in this work provide pure vibrational transition energies, which we believe are converged to the first/second digit after the decimal point (for the values expressed in wave numbers). The first few transitions are compared with the values derived from the available rotation-vibration experimental transitions. The only effects that are not accounted for in our calculations and that may contribute to the discrepancy between the predicted transition energies and the experimental ones are the relativistic and radiative corrections. Those, however, can be expected to be very small for a system like the HeH^+ ion. Thus, the present results for the pure vibrational transitions that have not yet been measured should provide a good set of predictions regarding the location of the spectral lines corresponding to the transitions.

ACKNOWLEDGMENTS

This work has been supported in part by the National Science Foundation. We thank Professor Jow-Tsong Shy for permission (given to M.M.) to use his unpublished HeH^+ data.

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