

## Convergence of Experiment and Theory on the Pure Vibrational Spectrum of $\text{HeH}^+$

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Very accurate quantum mechanical calculations of the pure vibrational spectrum of the  $\text{HeH}^+$  molecular ion are reported and compared with newly obtained pure vibrational transitions extracted from the available experimental data. The calculations are performed without assuming the Born-Oppenheimer approximation regarding separability of the nuclear and electronic motions and include the first order relativistic mass-velocity and Darwin corrections. For the two lowest transitions, whose experimental energies are established with the highest precision, the calculated and the experimental results show very good agreement.

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Modern gas phase measurements of molecular quantities such as rovibrational and electronic excitation energies, electron affinities, ionization potentials, bond dissociation, and atomization energies achieve nowadays the precision exceeding tenths or even hundredths of a wave number. This presents a challenge to quantum mechanical calculations because in order to reach such an accuracy, 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 has to be very accurately represented. Furthermore, even for small systems the relativistic effects need be taken into account.

In the present work we use the approach departing from the Born-Oppenheimer (BO) approximation whose development has been carried out for last several years in our research group [see [1–5] and references therein]. The main part of the development has been the use of correlated Gaussian functions that depend explicitly on the distances between the particles (nuclei and electrons) forming the molecule.

In this work we report the development and implementation of the algorithm for calculating electronic and nuclear mass velocity and Darwin corrections to the non-BO energy using an all-particle approach. To our knowledge, this is the first work where these relativistic corrections are computed for a molecular system with more than one electron within the non-BO framework. There have been very accurate calculations of molecular relativistic effects reported before [see, for example, Refs. [6,7]], but they only concerned the electronic corrections and all, except one on a single electron system [8], have been done within the BO approximation. The calculations presented in this work concern all bound states of the  $\text{HeH}^+$  ion with zero total angular momentum. Such states are usually called

“vibrational states” although, if the Born-Oppenheimer approximation is not assumed, the vibrational motion of the nuclei is coupled with the electronic motion and, strictly speaking, the vibrational quantum number,  $\nu$ , is not a good quantum number.

The hydrohelium cation  $\text{HeH}^+$ , whose first laboratory observation dates back to 1925 [9], is relevant to astrochemistry [10] since hydrogen and helium are the two most abundant elements in the universe. Apart from our recent work [5], all previous vibrational calculations of  $\text{HeH}^+$  in the electronic ground  $^1\Sigma^+$  state have been based on the Born-Oppenheimer potential energy curve and they were summarized in the work of Bishop and Cheung [11]. Since  $\text{HeH}^+$  has a relatively large permanent dipole moment, there have been some highly precise measurements of the vibration-rotational and pure rotational gas phase spectra of this system. We will refer to some of those measurements later in this work.

For several decades the most frequently used model system for testing the accuracy of high level quantum mechanical molecular calculations has been the hydrogen molecule. While the  $\text{HeH}^+$  ion has been used less frequently in such tests, it is a useful model for high level calculations, particularly those that include some account of the relativistic effects. This is due to the simplicity of the  $\text{HeH}^+$  electronic structure in the ground electronic state, which can be described as a helium atom slightly polarized by the proton. This polarization decreases with vibrational excitation. Our previous nonrelativistic non-BO calculations of  $\text{HeH}^+$  [5] yielded the transition energies involving the first four pure vibrational states that systematically overestimated the corresponding experimental transition energies by about  $0.07 \text{ cm}^{-1}$ . These differences inspired the present work on the relativistic corrections with the main goal of reducing the remaining theoretical or experimental discrepancy. The two largest relativistic correc-

tions, i.e., the ones due to the mass-velocity and Darwin effects, have been included in the present calculations. The remaining corrections related to the spin-orbit, orbit-orbit, and spin-spin interactions are expected to be at least by 1 order of magnitude smaller [due to the He-like electron distribution in  $\text{HeH}^+$ ; this conclusion is based on the calculations of the relativistic effects in He performed by Mitdal and Aashamar [12]] and have not been included.

We should also add that  $\text{HeH}^+$  is a system for which only a couple hundred rovibrational transitions have been assigned and no pure vibrational transitions have been measured. Thus, this important system is still “a work in progress” both in terms of the experimental and theoretical investigations. In this Letter we show how well these investigations are converging in determining the transition energies between the rotationless vibrational levels.

The total nonrelativistic Hamiltonian for  $\text{HeH}^+$  in the laboratory Cartesian coordinate system has the following form:

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

where the masses, charges, and positions of the four particles forming  $\text{HeH}^+$  are denoted as  $M_i$ ,  $Q_i$ , and  $\mathbf{R}_i$ , respectively. The first two particles are the nuclei of the He and H atoms, and the last two are the electrons. In the first step we transform the Hamiltonian (1) by separating the center-of-mass motion, thereby reducing the 4-particle problem to a 3-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,  $\mathbf{r}_0$ , 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 are 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 internal Hamiltonian,  $\hat{H}$ , is:

$$\hat{H} = -\frac{1}{2} \left( \sum_{i=1}^3 \frac{1}{m_i} \nabla_{\mathbf{r}_i}^2 + \sum_{i \neq j}^3 \frac{1}{M_1} \nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{r}_j} \right) + \sum_{i=1}^3 \frac{q_0 q_i}{r_i} + \sum_{i < j}^3 \frac{q_i q_j}{r_{ij}}, \quad (2)$$

where  $r_i = |\mathbf{r}_i|$  and  $r_{ij} = |\mathbf{R}_{j+1} - \mathbf{R}_{i+1}| = |\mathbf{r}_j - \mathbf{r}_i|$ . The separation of the internal Hamiltonian and the Hamiltonian of the motion of the center of mass is exact. The internal Hamiltonian (2) describes three pseudoparticles with charges  $q_i = Q_{i+1}$  and reduced masses  $m_i = M_1 M_{i+1} / (M_1 + M_{i+1})$  moving in the central potential of the charge of the reference particle.

In the calculation of the mass-velocity (MV) and the Darwin (D) corrections we start with respective Hamiltonians in the laboratory coordinate frame ( $\mathbf{R}$ ) [13]:

$$\hat{H}_{\text{MV}} = -\frac{1}{8c^2} \sum_{i=1}^4 \frac{1}{M_i^3} \nabla_{\mathbf{R}_i}^4, \quad (3)$$

$$\hat{H}_{\text{D}} = \frac{1}{8c^2} \sum_{i=1}^4 \frac{1}{M_i^2} \sum_{j \neq i}^4 \nabla_{\mathbf{R}_i}^2 \frac{Q_i Q_j}{R_{ij}}. \quad (4)$$

It should be noted that only spin-1/2 particles contribute to the D correction proportional to  $1/c^2$  (4) and the helium nucleus (zero spin) should be excluded from the sums in (4). However, for the sake of generality of the algorithm this was not explicitly done in the formula, but it was done by setting the inverse of the mass of the helium nucleus to zero in the calculation of the D correction which effectively eliminated the D interaction involving this particle.

Upon transformation of the laboratory coordinate system to the internal one, the Darwin Hamiltonian (4) can be expressed only in terms of the internal coordinates:

$$\hat{H}_{\text{D}}(\mathbf{r}) = \frac{1}{8c^2} \sum_{i=1}^3 \left[ \left( \frac{1}{M_1^2 + M_{i+1}^2} \right) \nabla_{\mathbf{r}_i}^2 \frac{q_0 q_i}{r_i} + \sum_{j \neq i}^3 \frac{1}{M_{i+1}^2} \nabla_{\mathbf{r}_i}^2 \frac{q_i q_j}{r_{ij}} \right], \quad (5)$$

while the mass-velocity Hamiltonian can be represented as a sum of three terms:

$$\hat{H}_{\text{MV}} = \hat{H}_{\text{MV}}(\mathbf{r}_0) + \hat{H}_{\text{MV}}(\mathbf{r}) + \hat{H}_{\text{MV}}(\mathbf{r}_0, \mathbf{r}),$$

where the term  $\hat{H}_{\text{MV}}(\mathbf{r})$ , relevant to the present calculations of the relativistic contribution to the internal energy, has the form:

$$\hat{H}_{\text{MV}}(\mathbf{r}) = -\frac{1}{8c^2} \left[ \frac{1}{M_1^3} \left( \sum_{i=1}^3 \nabla_{\mathbf{r}_i} \right)^4 + \sum_{i=1}^3 \frac{1}{M_{i+1}^3} \nabla_{\mathbf{r}_i}^4 \right]. \quad (6)$$

The calculation of the relativistic correction to the internal energy of the system is done separately for each state as the expectation value of the Hamiltonian representing the mass-velocity and Darwin contributions,

$$\hat{H}' = \hat{H}_{\text{MV}}(\mathbf{r}) + \hat{H}_{\text{D}}(\mathbf{r}),$$

with the non-BO wave function.

In our works concerning non-BO calculations on small diatomic molecular systems [3–5] we have shown that the explicitly correlated Gaussians (ECGs) involving functions with preexponential multipliers consisting of the internuclear distance,  $\mathbf{r}_1$ , raised to a non-negative even power,  $p_k$ :

$$\phi_k = r_1^{p_k} \exp[-\mathbf{r}'(A_k \otimes I_3)\mathbf{r}], \quad (7)$$

where  $\mathbf{r} = \{\mathbf{r}'_1, \mathbf{r}'_2, \mathbf{r}'_3\}'$ , are very effective in describing nonadiabatic, zero angular momentum states of diatomic systems with  $\sigma$  electrons. The above function is a one-center correlated Gaussian with exponential coefficients forming the symmetric, positive definite, matrix  $A_k$ .  $I_3$  in Eq. (7) is the  $3 \times 3$  identity matrix. In a more conventional way  $\phi_k$  can also be written as  $\phi_k = r_1^{p_k} \exp[-\sum_{i=1}^n \alpha_i^k r_i^2 - \sum_{i < j}^n \beta_{ij}^k r_{ij}^2]$ , where  $\alpha_i^k$  and  $\beta_{ij}^k$  are exponential coefficients that can be determined from the elements of matrix  $A_k$ .

The energy and the wave function for each state of  $\text{HeH}^+$  were obtained by minimizing the Rayleigh quotient:

$$E = \min \frac{c'H(\{p_k\}, \{A_k\})c}{c'S(\{p_k\}, \{A_k\})c} \quad (8)$$

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,  $\{p_k\}$ . Here,  $H$  and  $S$  are the Hamiltonian and the overlap matrices. The optimization was done separately for each state using an algorithm based on analytical derivatives of the energy,  $E(\{c_k\}, \{p_k\}, \{A_k\})$ , with respect to the  $A_k$  parameters. To achieve high accuracy we used 5400 basis functions for each state [this is by 900 more than used in [5]]. We believe that with this many functions in the basis the energies were converged to the 8th–9th decimal figure. The range of the preexponential powers,  $\{p_k\}$ , used was 0–250, and all the powers were partially optimized for each state.

After the wave functions for all 12 ( $v = 0, \dots, 11$ ) states were generated, we calculated the expectation values of  $\hat{H}'$  for each state and added them to the variational energies of the corresponding states. Those values were used to calculate the transition energies. In the calculations we used the following values for the nuclear masses:  $m_{\text{He}} = 7294.299\,536\,3m_e$  ( $^4\text{He}$  isotope),  $m_p = 1836.152\,672\,61m_e$  taken from CODATA 2002. Here,  $m_e$  stands for the mass of the electron.

Based on the available experimental data, only the frequencies ( $\nu_{v' \rightarrow v''}$ ) of the lowest three pure vibrational transitions ( $J = 0$ ), namely  $1 \rightarrow 0$ ,  $2 \rightarrow 1$ , and  $3 \rightarrow 2$ , of  $^4\text{HeH}^+$  can be estimated reliably. We used two independent estimation methods. The first one was based on fitting the microwave (MW) and infrared (IR) spectra of the four isotope variants of  $^4\text{HeH}^+$  to the radial parameters in the Herman-Ogilvie equation [14]:

$$\left[ -\frac{\hbar^2}{2m_0} \frac{d^2}{dx^2} + U_{vJ}(x) - E_{vJ} \right] \psi_{vJ}(x) = 0, \quad (9)$$

$$U_{vJ}(x) = \frac{B_0 J(J+1)[1 + \alpha(x) - \beta(x)]}{(1+x)^2} + V(x)[1 - \beta(x)] + V(x)' + E_{vJ}\beta(x) \quad (10)$$

including the adiabatic,  $V(x)'$ , the nonadiabatic rotational,  $\alpha(x)$ , and the vibrational,  $\beta(x)$ , corrections to the BO energy levels, and then calculating  $\nu_{1 \rightarrow 0}$ ,  $\nu_{2 \rightarrow 1}$ ,  $\nu_{3 \rightarrow 2}$ . The details of this method can be found in [5]. The results obtained are presented in Table I.

In the second method the vibrational frequencies were estimated by fitting the line positions of the separate bands  $1 \rightarrow 0$ ,  $2 \rightarrow 1$ , and  $3 \rightarrow 2$  of  $^4\text{HeH}^+$ , including  $R(J)$  and  $P(J)$  rovibrational transitions, to the Dunham's energy formula [22,23]:

$$E_{vJ} = \sum_{i,j} Y_{ij} \left( v + \frac{1}{2} \right)^i [J(J+1)]^j. \quad (11)$$

In this approach the frequencies of the vibrational transitions  $n \rightarrow m$  are directly obtained from the relationship:

$$\nu_{n \rightarrow m} = Y_{10}(v' \rightarrow v''). \quad (12)$$

The calculations were performed by using a weighted nonlinear least-squares routine with weights taken as the inverse squares of the uncertainties of the experimental data. To obtain the best set of the Dunham constants,  $Y_{ij}$ , fitted from the spectra, we used as the criteria: the smallest number of the fitted parameters consistent with the minimum value of the normalized standard deviation,  $\hat{\sigma}$ , the maximum value of the  $F$  statistics, and the optimal values of the estimated standard error,  $\sigma_i$ , of each fitted parameter  $i$  and of the coefficient,  $cc(i, j)$ , correlating parameters  $i$  and  $j$ . The results of these calculations are also presented in Table I. The uncertainty shown in parentheses is the estimated standard deviation in the units of the last quoted digit of the values of the fitted Dunham constants.

The discrepancy  $\Delta\nu_{3 \rightarrow 2} = 0.0452 \text{ cm}^{-1}$  in the values of the  $\nu_{3 \rightarrow 2}$  vibrational frequency calculated by the two specified methods is due to a small number of available line positions (only 11) used in the calculation. Hence, in this case we can only specify the range for this frequency as  $\nu_{3 \rightarrow 2} \in [2295.5340(61) - 2295.5792]$ . The differences in the values of the remaining frequencies  $\Delta\nu_{1 \rightarrow 0} = 0.0018 \text{ cm}^{-1}$  and  $\Delta\nu_{2 \rightarrow 1} = 0.001 \text{ cm}^{-1}$  are less than the experimental uncertainties of the spectral data used in the calculations ( $0.002 - 0.003 \text{ cm}^{-1}$ ). The only exception is the data (7 lines) of Shy [20] obtained with the accuracy of  $0.0006 \text{ cm}^{-1}$ .

TABLE I. Dunham's spectral parameters (in  $\text{cm}^{-1}$ ) fitted to the  $^4\text{HeH}^+$   $0 \rightarrow 1$ ,  $1 \rightarrow 2$ ,  $2 \rightarrow 3$  vibrational bands.

$Y_{ij}$	$v = 0 \rightarrow 1$	$v = 1 \rightarrow 2$	$v = 2 \rightarrow 3$
$Y_{10}$	2910.9572(7)	2604.1482(12)	2295.5340(61)
$Y_{11}$	-2.718 696(88)	-2.74063(34)	-2.79342(49)
$Y_{12} \times 10^4$	3.580(28)	2.24(18)	-1.04(13)
$Y_{13} \times 10^7$	-4.37(26)	-3.4(38)	3.4(14)
$Y_{14} \times 10^8$		-1.29(47)	-0.565(52)
$Y_{15} \times 10^{11}$		-1.05(21)	
$Y_{01}$	34.91777(13)	34.95109(80)	35.0828(15)
$Y_{02} \times 10^{-2}$	-1.63857(32)	-1.6261(37)	-1.5353(41)
$Y_{03} \times 10^{-6}$	5.984(34)	8.05(66)	3.60(47)
$Y_{04} \times 10^{-9}$	-2.06(15)	-5.0(53)	13.0(21)
$Y_{05} \times 10^{-11}$		-9.1(32)	-1.05(21)
$Y_{06} \times 10^{-13}$		1.74(48)	
$\hat{\sigma}$	0.606	1.049	0.148
$J_{\min} - J_{\max}$	0–14	0–20	4–18
Lines	22	25	11
$\nu_{n \rightarrow m}$	2910.9572(7)	2604.1482(12)	2295.5340(61)
$\nu_{n \rightarrow m}^a$	2910.9590	2604.1472	2295.5792
data	[15–20]	[15,17–21]	[19,20]

<sup>a</sup>Frequencies obtained by fitting the MW and IR spectra of four isotopic variants of  $\text{HeH}^+$  to the radial parameters in the Eq. (9).

TABLE II. Total non-BO energies ( $E_{\text{non-BO}}$ ), mass-velocity corrections (MV), Darwin corrections,  $v + 1 \rightarrow v$  vibrational frequencies calculated without ( $\Delta E_{\text{non-BO}}$ ) and with ( $\Delta E_{\text{non-BO+rel}}$ ) inclusion of relativistic corrections, and first three vibrational frequencies extracted from experimental data using two different methods of extrapolation ( $\Delta E_{\text{exp}}^a$  and  $\Delta E_{\text{exp}}^b$ , respectively). The energies and corrections are given in a.u., the frequencies in  $\text{cm}^{-1}$ .

$v$	$E_{\text{non-BO}}$	MV	Darwin	$\Delta E_{\text{non-BO}}$	$\Delta E_{\text{non-BO+rel}}$	$\Delta E_{\text{exp}}^a$	$\Delta E_{\text{exp}}^b$
0	-2.971 078 463 6	$-7.12801 \times 10^{-4}$	$5.85088 \times 10^{-4}$	2911.0189	2911.0007	2910.959	2910.957
1	-2.957 814 885 4	$-7.11099 \times 10^{-4}$	$5.83303 \times 10^{-4}$	2604.2064	2604.1676	2604.147	2604.148
2	-2.945 949 248 2	$-7.10031 \times 10^{-4}$	$5.82058 \times 10^{-4}$	2295.6365	2295.5787	2295.579	2295.534
3	-2.935 489 558 6	$-7.09481 \times 10^{-4}$	$5.81245 \times 10^{-4}$	1982.1338	1982.0562		
4	-2.926 458 292 7	$-7.09571 \times 10^{-4}$	$5.80981 \times 10^{-4}$	1660.4533	1660.3559		
5	-2.918 892 711 0	$-7.10185 \times 10^{-4}$	$5.81152 \times 10^{-4}$	1327.9067	1327.7860		
6	-2.912 842 322 8	$-7.11474 \times 10^{-4}$	$5.81891 \times 10^{-4}$	984.4980	984.3599		
7	-2.908 356 619 8	$-7.13281 \times 10^{-4}$	$5.83069 \times 10^{-4}$	639.3467	639.1959		
8	-2.905 443 541 7	$-7.15525 \times 10^{-4}$	$5.84625 \times 10^{-4}$	327.4922	327.3615		
9	-2.903 951 377 4	$-7.17684 \times 10^{-4}$	$5.86189 \times 10^{-4}$	116.2220	116.1487		
10	-2.903 421 831 1	$-7.18995 \times 10^{-4}$	$5.87166 \times 10^{-4}$	24.4368	24.4099		
11	-2.903 310 488 9	$-7.19492 \times 10^{-4}$	$5.87541 \times 10^{-4}$				
Unbound	-2.903 304 556 5						

The total and transition energies for all 12 bound vibrational states of  $\text{HeH}^{-1}$  with zero total angular momentum obtained in the non-BO calculations are presented in Table II. Both nonrelativistic results and results including the relativistic corrections are shown. All transition energies corrected for the relativistic effects are lower than their uncorrected counterparts. The largest shift of  $-0.1508 \text{ cm}^{-1}$  due to the relativistic corrections occurs for the  $8 \rightarrow 7$  transition. It is clear that for all transitions the inclusion of relativistic corrections change the frequencies by much more than their respective experimental errors. The comparison between the calculated transition frequencies and the experimental results for the first three transitions is also shown in Table II. As mentioned, only for the first two transitions did the experimental results obtained using both estimation methods agree to high precision. For those two transitions the relativistic corrections bring the predicted frequencies noticeably closer to the experimental values. Although adding the relativistic correction to the third transition ( $3 \rightarrow 2$ ) also improves the result, there is a discrepancy between the two extrapolated experimental values, making this case less reliable.

In conclusion, it is clear from the results presented here that theoretical calculations with an approach that does not assume the BO approximation and includes some relativistic effects (of the order of  $\alpha^2$ ) are capable of generating results whose accuracy matches the accuracy of the experimental measurements. It is also clear that, while in the calculations all 11 pure vibrational transitions are predicted, only two lowest transitions are reliably established on the experimental side.

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- [1] M. Cafiero, S. Bubin, and L. Adamowicz, *Phys. Chem. Chem. Phys.* **5**, 1491 (2003).
- [2] S. Bubin, M. Cafiero, and L. Adamowicz, *Adv. Chem. Phys.* **131**, 377 (2005).
- [3] D. B. Kinghorn and L. Adamowicz, *Phys. Rev. Lett.* **83**, 2541 (1999).
- [4] S. Bubin and L. Adamowicz, *J. Chem. Phys.* **118**, 3079 (2003).
- [5] M. Pavanello, S. Bubin, M. Molski, and L. Adamowicz, *J. Chem. Phys.* **123**, 104306 (2005).
- [6] G. Tarczay, A. G. Császár, W. Klopper, and H. M. Quiney, *Mol. Phys.* **99**, 1769 (2001).
- [7] O. L. Polyansky, A. G. Császár, S. V. Shirin, N. F. Zobov, P. Barletta, J. Tennyson, D. W. Schwenke, and P. J. Knowles, *Science* **299**, 539 (2003).
- [8] R. E. Moss and L. Valenzano, *Mol. Phys.* **101**, 2635 (2003).
- [9] T. R. Hogness and E. G. Lunn, *Phys. Rev.* **26**, 44 (1925).
- [10] D. Galli and F. Palla, *Astron. Astrophys.* **335**, 403 (1998).
- [11] D. M. Bishop and L. M. Cheung, *J. Mol. Spectrosc.* **75**, 462 (1979).
- [12] J. Mitdal and K. Aashamar, *Phys. Norv.* **2**, 99 (1967)
- [13] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Plenum, New York 1977).
- [14] R. M. Herman and J. F. Ogilvie, *Adv. Chem. Phys.* **103**, 187 (1998).
- [15] D. E. Tolliver, G. A. Kyrala, and W. H. Wing, *Phys. Rev. Lett.* **43**, 1719 (1979).
- [16] P. Bernath and T. Amano, *Phys. Rev. Lett.* **48**, 20 (1982).
- [17] C. E. Blom, K. Möller, and R. R. Filgueira, *Chem. Phys. Lett.* **140**, 489 (1987).
- [18] M. W. Crofton, R. S. Altman, N. N. Haese, and T. Oka, *J. Chem. Phys.* **91**, 5882 (1989).
- [19] J. Purder, S. Cavis, C. E. Blom, and M. C. van Hemert, *J. Mol. Spectrosc.* **153**, 701 (1992).
- [20] Unpublished data; it includes 6 lines of  $v = 1 \rightarrow 0$ ,  $2 \rightarrow 1$ ,  $3 \rightarrow 2$ , for  $^4\text{HeH}^+$  measured with the accuracy of  $0.0006 \text{ cm}^{-1}$  by J.-T. Shy.
- [21] Z. Liu and P. B. Davies, *J. Chem. Phys.* **107**, 337 (1997).
- [22] J. L. Dunham, *Phys. Rev.* **41**, 713 (1932).
- [23] J. L. Dunham, *Phys. Rev.* **41**, 721 (1932).