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Fundamental vibration frequency and rotational structure of the first excited vibrational level of the molecular helium ion (He_2^+)

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The term values of rotational levels of the first excited vibrational state of the electronic ground state of He_2^+ with rotational quantum number $N^+ \leq 13$ have been determined with an accuracy of $1.2 \times 10^{-3} \text{ cm}^{-1}$ ($\sim 35 \text{ MHz}$) by MQDT-assisted Rydberg spectroscopy of metastable He_2 . Comparison of the experimental term values with the most accurate *ab initio* results for He_2^+ available in the literature [W.-C. Tung, M. Pavanello, and L. Adamowicz, *J. Chem. Phys.* **136**, 104309 (2012)] reveals inconsistencies between theoretical and experimental results that increase with increasing rotational quantum number. The fundamental vibrational wavenumber of He_2^+ was determined to be $1628.3832(12) \text{ cm}^{-1}$ by fitting effective molecular constants to the obtained term values.

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I. INTRODUCTION

Ab initio calculations of the properties of few-electron molecules are currently in a phase of rapid progress and methodological change [1–16]. To reach the high accuracy required for the comparison with the latest experimental results, it now appears advantageous to abandon the traditional approach starting with calculations of Born-Oppenheimer potential-energy functions, or surfaces, and of adiabatic and nonadiabatic corrections, followed by a perturbative treatment of relativistic and radiative corrections. Until recently, this approach could adequately reproduce energies measured by high-resolution spectroscopy [17–21]. Puchalski *et al.* [9] recently found out that the evaluation of the relativistic corrections with adiabatic wavefunctions was not sufficiently accurate to account for the experimental results on H_2 [17]. This problem has very recently been overcome in H_2 by the direct (also referred to as pre-Born-Oppenheimer) solution of the four-particle nonrelativistic Schrödinger equation to obtain nonrelativistic energies and to use the corresponding nonadiabatic wavefunctions to calculate the relativistic corrections [10, 11]. An alternative approach would consist of a direct solution of the four-particle relativistic Dirac equations.

The natural next step in this development is to gradually increase the number of particles (electrons or nuclei) and an obvious system is the three-electron molecule He_2^+ . Reference spectroscopic data on He_2^+ are, however, very scarce and are limited to (i) intervals between highly excited vibrational levels of the $X^+ 2\Sigma_u^+$ state and the lowest vibrational levels of the $A^+ 2\Sigma_g^+$ state measured by Carrington and coworkers [22], (ii) several infrared transitions connecting rotational levels of the $v^+ = 0$ and $v^+ = 1$ levels of $^3\text{He}^4\text{He}^+$ [23, 24], and (iii) the positions of the $N^+ = 1, 3, \dots, 19$ rotational levels [25–27] of the ground vibronic level of $^4\text{He}_2^+$

and their spin-rotational splitting [28], determined from the analysis of high Rydberg states of He_2 . Both the spin-rotational splittings and the rotational term values revealed discrepancies with the values obtained by the latest calculations [14, 24], although significant progress in the calculation of nonadiabatic corrections could be achieved very recently [29].

We report here on a measurement of the fundamental vibrational interval ($v^+ = 1 - v^+ = 0$) in the ground electronic state and of the positions of the ($v^+ = 1$, $N^+ = 1 - 13$) rotational levels of $^4\text{He}_2^+$, which almost doubles the experimental data set available for comparison with *ab initio* calculations. We hope that these new data will be useful for comparison with theoretical results and stimulate the development of adequate theoretical tools.

II. EXPERIMENTAL PROCEDURE

The measurements were performed with the experimental setup described in Refs. [26, 27, 30]. In brief, a supersonic beam containing metastable helium molecules in the $a^3\Sigma_u^+$ state (called He_2^* hereafter) was produced by striking an electric discharge through an expansion of pure helium gas at the exit of a pulsed valve [31]. The body of the valve was cooled with liquid nitrogen to a temperature of 77 K, resulting in a supersonic beam with a velocity of approximately 1000 m/s [32]. The molecular beam was collimated with a 2-mm-diameter skimmer and, after about 50 cm of free flight, crossed the pulse-amplified and frequency-doubled output (pulse length of $\approx 5 \text{ ns}$) of a single-mode continuous-wave (cw) ring dye laser [33] at right angle on the axis of a cylindrically symmetric stack of electrodes for the application of ionization and extraction electric fields. The fundamental frequency of the laser was calibrated to an accuracy of 20 MHz (1σ) by coupling a fraction of the pulse-amplified output of the ring laser into a wavemeter (HighFinesse WS7). Transitions from the metastable $a^3\Sigma_u^+$ ($v'' = 1, N''$) levels to high- n Rydberg states were detected by monitoring the

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He_2^+ ions produced by field ionization with a pulsed electric field of 250 V/cm, applied 3.5 μs after the laser excitation pulse.

The spectra were simplified by applying a 1.7-V/cm electric field immediately after photoexcitation but before the field-ionization pulse. This first “discrimination” pulse was used to ionize the highest Rydberg states ($n > 140$) converging on the $X^+ 2\Sigma_u^+$ ($v^+ = 0$) vibrational ground state of He_2^+ that would otherwise overlap with the Rydberg series converging on rotational levels of the $X^+ 2\Sigma_u^+$ ($v^+ = 1$) vibrational state of He_2^+ . Indeed, the $v'' = 0 \rightarrow v^+ = 0$ and $v'' = 1 \rightarrow v^+ = 1$ thresholds have similar energies. The discrimination pulse also swept all ions produced by direct ionization or rapid autoionization (prompt ions) out of the photoexcitation volume. Stray electric fields were determined by recording spectra in the presence of different applied potentials across the electrode stack and fitting the observed Stark shifts to a quadratic polynomial and were compensated to a level of about 1 mV/cm along the symmetry axis of the electrode stack [34]. Stray magnetic fields were suppressed to below 10 mG by two concentric mu-metal shields placed around the electrode stack.

III. RYDBERG SERIES OF He_2 AND MULTICHANNEL QUANTUM-DEFECT THEORY EXTRAPOLATION

The $X^1\Sigma_g^+$ electronic ground state of $^4\text{He}_2$ supports a single rovibrational level with a binding energy of only 33.6(6) MHz [35] and a mean internuclear distance of 54(4) Å [36]. In contrast, the $X^+ 2\Sigma_u^+$ electronic ground state He_2^+ ion is strongly bound and possesses many rovibrational states. The stability of He_2^+ implies the existence of singlet and triplet Rydberg series of He_2 that converge on the different rovibrational levels of the ion. All bound states of He_2 other than the single level of the electronic ground state are Rydberg states [37]. The lowest Rydberg state of He_2 , He_2^* , has a lifetime of 18 s [38] because its radiative decay to the $X^1\Sigma_g^+$ electronic ground state is spin forbidden. The lowest rotational levels of the vibrational ground and first excited states of He_2^* are schematically depicted in Fig. 1 along with the np Rydberg series converging on the corresponding rovibrational levels of the He_2^+ ion. The bosonic ^4He nuclei exclude the existence of rotational states with even rotational quantum number N in the $a^3\Sigma_u^+$ state of the neutral molecule and the $X^+ 2\Sigma_u^+$ state of the ion. In the following, double primed symbols, unprimed symbols, and symbols with a superscript “+” are used to indicate the quantum numbers of He_2^* , He_2 Rydberg states, and $\text{He}_2^+(X^+ 2\Sigma_u^+)$, respectively.

The level structure of He_2^* is best described using Hund’s angular-momentum coupling case (b), where the total angular momentum excluding spin $\vec{N}''$ couples to the total electron spin $\vec{S}''$ to form the total angular momentum $\vec{J}''$. The spin-spin and spin-rotation interactions

Figure 1. Energy-level diagram showing the lowest rotational levels of the ground and first excited vibrational states of He_2^* and the triplet np Rydberg series of He_2 converging on the lowest rotational levels of He_2^+ ($X^+ 2\Sigma_u^+$, $v^+ = 0, 1$). Red and yellow arrows represent the $npN_N^+ \leftarrow N''$ series with $N^+ = N''$ and $N = N^+, N^+ + 1$ and the $npN_N^+ \leftarrow N''$ series with $N^+ = N'' - 2$ and $N = N^+ + 1$, respectively, that were used to determine ionization thresholds and rotational structure of the vibrational ground state of He_2^* and to derive the rotational term values of He_2^+ ($X^+ 2\Sigma_u^+$, $v^+ = 0$) in Refs. [26, 27]. Curved blue and green arrows indicate the $npN_N^+ \leftarrow N''$ series that undergo rapid rotational autoionization above the $N^+ - 2$ threshold and vibrational autoionization above the $v^+ = 0$ threshold. The fine structure of the energy levels is not visible on the scale of the figure and is shown exaggerated for the lowest rotational state of He_2^* only.

split each rotational level into three components with $J'' = N'', N'' \pm 1$. The np Rydberg states that are accessed in our experiment are best described using Hund’s coupling case (d). The rotational angular momentum of the ionic core $\vec{N}^+$ couples to the orbital angular momentum of the Rydberg electron $\vec{\ell}$ to form $\vec{N}$, which in turn couples to the total electron spin $\vec{S}$ resulting in the total angular momentum vector $\vec{J}$. The level structure of the He_2^+ ion also follows a Hund’s case (b) coupling scheme: $\vec{N}^+$ couples to the electron spin $\vec{S}^+$ of the unpaired electron to form $\vec{J}^+$.

Rydberg series converging on a particular (v^+, N^+) rovibrational level of the $X^+ 2\Sigma_u^+$ electronic ground state of He_2^+ are approximately described by Rydberg’s formula

$$\tilde{\nu}_{n\ell} = \frac{E_1 + E_{\text{rv}}^+ - E_{\text{rv}}''}{hc} - \frac{\mathcal{R}_{\text{He}_2}}{(n - \delta_\ell)^2}, \quad (1)$$

where $\tilde{\nu}_{n\ell}$ represents the spectral position of the Rydberg states of principal and orbital angular-momentum quantum numbers n and ℓ , respectively, and quantum defect δ_ℓ . The quantities $\mathcal{R}_{\text{He}_2}$ and E_1 represent the mass-corrected Rydberg constant for He_2 and the adiabatic ionization energy of He_2^* , corresponding to the energy difference between the $X^+ 2\Sigma_u^+(v^+ = 0, N^+ = 1)$ level of He_2^+ and the $a^3\Sigma_u^+(v'' = 0, N'' = 1)$ metastable level, respectively. E_{rv}^+ and E_{rv}'' are the rovibrational energies of the He_2^+ ion core and of He_2^* with respect to the $(v^+ = 0, N^+ = 1)$ and $(v'' = 0, N'' = 1)$ levels, respectively. Although Rydberg's formula accurately describes the essentially unperturbed $npN_{N=N^+}^+$ series, it does not account for the interactions between series of the same N value that converge on different rovibrational states of He_2^+ . These interactions give rise to spectral perturbations below, and to rotational autoionization above, the $N^+ = N - 1$ thresholds. Vibrational channel interactions lead to additional perturbations and to vibrational autoionization above the $v^+ = 0$ ionization thresholds. Both rotational and vibrational channel interactions can be accounted for in the framework of multichannel quantum-defect theory [39].

The quantum-defect parameters for the *gerade* triplet np and nf Rydberg states of He_2 , derived by Sprecher *et al.* [25], were adopted without change for the extrapolation of the Rydberg series. In Ref. [25], internuclear-distance(R)- and energy(ϵ)-dependent η eigenquantum-defect matrices were extracted from data available in the literature on np and nf Rydberg levels with n in the range $2 - 39$, $v^+ \leq 2$, and $N^+ \leq 19$ in a least-squares-fit procedure. High- n Rydberg states were not included in the fit, because the level energies of high- n Rydberg states are insensitive to adjustments of the quantum defects (see Ref. [25] for details). The range of principal quantum numbers used in the present work ($n = 100 - 130$) for the extrapolation represents a compromise between selecting the highest possible n states that are not significantly affected by stray electric fields. The Rydberg-series extrapolation was performed using the MQDT program developed by Christian Jungen [39]. The ionization thresholds, in combination with the rovibrational term values of He_2^* available in Refs. [40, 41], enabled us to determine the term values of the rotational levels of the first excited vibrational state of He_2^+ for comparison with the *ab initio* calculations of Tung *et al.* [14].

IV. RESULTS

The transitions observed in our spectra connect the Hund's case (b) levels of He_2^* to Hund's case (d) Rydberg levels (see Fig. 1) and are labeled as $np(v^+, N^+)_N \leftarrow (v'', N'')$. The dominant Rydberg series in the spectrum

of He_2 are those with $N^+ = N''$. There are three such series converging on each rotational level of He_2^+ with $N = N^+, N^+ \pm 1$. However, all npN_{N+1}^+ Rydberg states with $N^+ > 1$ located above the $N^+ - 2$ and $v^+ = 0$ ionization thresholds are subject to rapid rotational autoionization, because of the strong coupling, indicated by the curved arrows in Fig. 1, between channels of the same value of N , but differing in N^+ by 2 [25, 31]. The corresponding transitions are strongly broadened and thus not easily observable in our high-resolution spectra. Because the rotational channel interactions are stronger than the vibrational channel interactions [39], vibrational autoionization widths for a given value of n are much narrower than the rotational autoionization widths.

Rydberg series converging on the first excited vibrational state of He_2^+ could be recorded in the range $n = 100 - 130$. Below the $N^+ - 2$ ionization thresholds, the rotational autoionization of the npN_{N+1}^+ Rydberg states is suppressed for energetic reasons. In this region, the coupling between the npN_{N+1}^+ and $np[N^+ - 2]_{N+1}$ channels leads to strong perturbations through which the O-branch-type transitions with $N^+ = N'' - 2$ may become observable by borrowing intensity from the strong Q-type transitions with $N'' = N^+$. These transitions enable the determination of the relative positions of the $N'' - 2$ and N'' levels by building combination differences and are required to derive the relative term values of the $N^+ - 2$ and N^+ levels, as explained in Ref. [27]. Unfortunately, we did not observe such transitions for Rydberg series converging on rotational levels of the $v^+ = 1$ vibrational state of He_2^+ nor were we able to record transitions connecting the vibrational ground state of He_2^* to Rydberg states converging on the first excited vibrational level of He_2^+ because of the near-diagonal Franck-Condon factors of the $X^+ \leftarrow a$ photoionizing transition. Term values of the rovibrational levels of He_2^* could therefore not be inferred from our Rydberg spectra but were obtained by building combination differences using the $b^3\Pi_g - a^3\Sigma_u^+$ and $c^3\Sigma_g^- - a^3\Sigma_u^+$ transition wavenumbers reported by Bernath and coworkers [40, 41], and the fine-structure constants derived in Ref. [41] (see Table I). Transitions between fine-structure components of the rovibrational levels of He_2^* and Rydberg states are governed by the selection rule $\Delta J = J - J'' = N - N'' = \Delta N$ [28], so that the $np(v^+, N^+)_N \leftarrow (v'', N'')$ transitions all appear as triplets in the spectrum.

The fine structure that is observed in the spectra closely resembles that of the initial metastable state because the fine structure intervals of He_2^* are much larger than those of the Rydberg states [28]. We used the fine-structure constants of the $v'' = 1$ level of He_2^* reported by Focsa *et al.* [41] to determine the spin-rotation interval in He_2^* . The fine-structure of the Rydberg levels was obtained by scaling the fine-structure constants of the $v^+ = 0$ level of He_2^+ [28], according to the calculation of the fine structure of $^3\text{He}^4\text{He}^+$ in the ground and first excited vibrational state by Yu, Wing and Adamowicz [24]. In combination with the $\Delta N = \Delta J$ angular momentum

Figure 2. Spectra of the $np(v^+ = 1, N^+)_N \leftarrow a^3\Sigma_u^+(v'' = 1, N'')$ series of He_2 with $N^+ = N'' \leq 13$, $N = N^+, N^+ + 1$ and n around 115. The upper and lower assignment bars in each spectrum correspond to the $N = N^+ + 1$ and N^+ series, respectively.

selection rule mentioned above, these spin-rotation intervals enabled the derivation of the triplet splitting of the Rydberg transitions in the spectrum. Three Gaussian functions, separated by these splittings and with relative intensities given by the $2J'' + 1$ degeneracy factors, were used to convert each observed triplet into its “fine-structure-free” center of gravity.

The spectra of the $np(v^+ = 1, N^+ = N'')_N \leftarrow (v'' = 1, N'')$ Rydberg series with $N'' \leq 13$ and n around 115 are depicted in Fig. 2 and the corresponding transition wavenumbers are listed in Table II. The Rydberg series converging on the $N^+ = 5$ and 9 rotational levels of $\text{He}_2^+ X^+ {}^2\Sigma_u^+(v^+ = 1)$ could not be observed because they overlap with the much stronger $np(0, 15) \leftarrow (0, 15)$ and $np(0, 17) \leftarrow (0, 17)$ series of lower principal quantum number n . The spectra presented in Fig. 2 show at least one of the two expected series. In some spectra, such as that of the $np(1, 7)_{7,8} \leftarrow (1, 7)$ transitions, the two different series are clearly distinguishable, whereas they almost completely overlap in the spectra of $np(1, 3)_{3,4} \leftarrow (1, 3)$ and $np(1, 11)_{11,12} \leftarrow (1, 11)$ series.

In general, the spectral intensity of the perturbed

$N = N^+ + 1$ series increases with increasing n value, which is particular apparent for the transitions of the $np(1, 7)_8 \leftarrow (1, 7)$ and $np(1, 13)_{14} \leftarrow (1, 13)$ series. This observation implies that the lifetimes of Rydberg states with $n \lesssim 100$ and $N = N^+ + 1$ are too short to be observed by delayed pulsed-field ionization and that these states should appear in the prompt-ion signal. However, the prompt signal related to Rydberg states converging on rotational states of the $v^+ = 0$ threshold completely obscures the much weaker signal from series belonging to the $v^+ = 1$ thresholds. The short lifetimes of these states explain our inability to observe the $np(1, N^+ - 2)_{N^+-1} \leftarrow (1, N^+)$ Rydberg series in the pulsed-field ionization spectra. In contrast, the almost unperturbed Rydberg states with $N = N^+$ have lifetimes of at least 3.5 μs . Surprisingly, transitions to the long-lived $np7_7$ and $np13_{13}$ Rydberg states have fitted linewidths of ~ 300 MHz as compared to linewidths of ~ 200 MHz observed for transitions to Rydberg states belonging to the other series. This observation might be an indication of an electric-field induced mixing of these p levels with nearby f levels. In the global fit, transitions

Table I. Rovibrational term values of the $a^3\Sigma_u^+(v'' = 1)$ state of He_2 derived from combination differences of the $b^3\Pi_g - a^3\Sigma_u^+$ and $c^3\Sigma_g^+ - a^3\Sigma_u^+$ system using transition wavenumbers reported by Refs. [40] and [41], respectively, and the fine-structure constants of Ref. [41] (2nd column). The 4th column lists rovibrational term values of the $X^+2\Sigma_u^+(v^+ = 1)$ ground state of He_2^+ derived in this study from an MQDT-assisted extrapolation of the Rydberg series. For comparison, the term values of the $X^+2\Sigma_u^+(v^+ = 1)$ state of $^4\text{He}_2^+$ calculated *ab initio* by Tung *et al.* [14] are shown in the 5th column. All values are given in cm^{-1} .

N''	$E''_{\text{rv}}(N'')$ Refs. [40, 41]	N^+	$E_{\text{rv}}^+(N^+)$ This work	Ref. [14]
1	1731.6782(7)	1	1627.9318(12)	1627.929
3	1805.0861(4)	3	1696.6096(12)	1696.607
5	1936.9379(4)	5		1819.964
7	2126.7459(4)	7	1997.5633(12)	1997.553
9	2373.8123(4)	9		2228.732
11	2677.2308(4)	11	2512.6871(12)	2512.668
13	3035.8964(4)	13	2848.3690(12)	2848.342

to $np7_7$ and $np13_{13}$ Rydberg states were therefore given half the weight of the other observed transitions.

The data set does not contain series converging on the $N^+ = 5, 9$, and 15 thresholds. These series can however perturb the $N = 4, 8$, and 14 series converging on the $N^+ = 3, 7$, and 13 thresholds. Although the spectra presented in Fig. 2 do not show evidence of such perturbations, we adopted a two-step approach to account for this effect. In a first fit, all term values of rovibrational levels of He_2^+ with $v^+ = 1$ and $N^+ \leq 15$ were determined from optimizing a set of effective rotational constants for the $v^+ = 1$ state. In the second fit, the $(v^+ = v'', N^+ = N'')$ ionization thresholds of the $(v'' = 1, N'' = 1, 3, 7, 11, \text{ and } 13)$ levels were adjusted individually, while the ionization thresholds of the $(v'' = 1, N'' = 5, 9, \text{ and } 15)$ levels were kept fixed to their values as determined in the first fit. The relative positions of the ionic rovibrational levels obtained in the second fit are listed in the fourth column of Table I, where they are compared with the results of the *ab initio* calculations of Tung *et al.* [14] (last column). The differences between the observed and calculated line positions of the Rydberg transitions used in the fit are shown in Table II. These residuals seem to show a systematic trend for the series converging on the $N^+ = 7$ and 13 thresholds. We attribute this effect to a small electric stray field that is perpendicular to the symmetry axis of the electrode stack and that mixes the p and f Rydberg states. Excluding the affected $np(1,7)_7 \leftarrow (1,7)$ and $np(1,13)_{13} \leftarrow (1,13)$ series from the fit changes the $N^+ = 7$ and 13 thresholds by -35 and -15 MHz, respectively. In addition, resampling the residuals of our full data set 200 times using the model-based-bootstrap method [42] reproduces the fit results within 20 MHz. Consequently, this effect does not significantly affect the results presented in Table I.

Table III summarizes the main sources of systematic

and statistical uncertainties in the determination of the absolute and relative transition wavenumbers. The main source of the relative statistical uncertainty comes from forming combination differences to obtain the rovibrational term values of He_2^+ (~ 20 MHz) and from the relative wavenumber calibration (25 MHz, resulting from small fluctuations of the wavemeter readings for spectra recorded on different days [27]). The uncertainty in the fitted line positions of individual Rydberg transitions is on the order of $10 - 20$ MHz, but the contribution to the absolute and relative statistical error is ~ 5 MHz because about 10 transitions were used to extrapolate each series. The final contribution to the absolute and relative statistical uncertainty comes from the MQDT extrapolation (~ 10 MHz). Assuming that all error sources are independent results in a total statistical uncertainty of the rovibrational term values of 35 MHz. The systematic uncertainty of the transition wavenumbers is dominated by the absolute calibration error of the wavemeter (40 MHz). However, this error cancels out in the relative uncertainty of the rotational term values when building combination differences between the different thresholds. The DC Stark shift, induced by stray electric fields perpendicular to the symmetry axis of the electrode stack and prompt ions, also contributes to the absolute and relative systematic uncertainty. Because the extrapolation is performed using Rydberg states of similar n value, this contribution is partially canceled in the reconstruction of the relative rovibrational term values.

Figure 3. Differences between experimental (this work) and theoretical rovibrational term values (from Ref. [14]) in the $X^+2\Sigma_u^+(v^+ = 1)$ state of He_2^+ (full squares) with respect to the $v^+ = 0, N^+ = 1$ level. For comparison, the experimental results obtained by Semeria *et al.* [27] for the vibrational ground state of He_2^+ are plotted as open squares. The gray area represents the estimated uncertainty of the theoretical results reported in Ref. [14].

Table II. Observed transitions from the $a^3\Sigma_u^+$ ($v'' = 1, N''$) state of $^4\text{He}_2$ to the npN_N^+ Rydberg states belonging to series converging to the $X^+{}^2\Sigma_u^+$ ($v^+ = 1, N^+$) states of $^4\text{He}_2^+$ and comparison with the results of MQDT calculations. The symbol Δ represents the difference between observed and calculated line positions ($\Delta = \tilde{\nu}_{\text{obs.}} - \tilde{\nu}_{\text{calc.}}$). All values are given in cm^{-1} . Missing entries correspond to transitions that were not observed or to strongly blended transitions.

n	$(1, 1) \rightarrow np(1, 1)_1$		$(1, 1) \rightarrow np(1, 1)_2$		$(1, 3) \rightarrow np(1, 3)_4$		$(1, 7) \rightarrow np(1, 7)_7$	
	$\tilde{\nu}_{\text{obs}}$	Δ	$\tilde{\nu}_{\text{obs}}$	Δ	$\tilde{\nu}_{\text{obs}}$	Δ	$\tilde{\nu}_{\text{obs}}$	Δ
92			34 184.503 36	0.000 07				
93			34 184.775 02	-0.001 20				
94			34 185.039 65	-0.000 65				
...								
108	34 188.039 86	0.000 07	34 188.064 51	0.000 64	34 183.323 05	-0.000 66		
109	34 188.211 20	-0.000 74	34 188.233 71	0.000 12	34 183.495 61	0.001 00		
110	34 188.379 77	0.000 36	34 188.399 55	0.000 64	34 183.660 70	0.000 24		
111	34 188.541 81	-0.000 56	34 188.560 05	0.000 14	34 183.821 43	-0.001 01		
112					34 183.979 05	-0.000 82		
113	34 188.856 47	0.001 06	34 188.869 87	0.000 49	34 184.132 56	-0.000 53	34 163.423 37	0.002 09
114					34 184.281 95	-0.000 31	34 163.573 13	0.001 78
115	34 189.151 55	-0.000 70	34 189.163 52	0.000 63	34 184.427 36	-0.000 14	34 163.719 68	0.001 82
116	34 189.294 53	-0.000 41	34 189.304 67	0.000 70	34 184.569 04	0.000 09	34 163.862 07	0.001 67
117					34 184.707 20	0.000 49	34 164.000 97	0.001 60
118					34 184.842 27	0.001 36	34 164.136 65	0.001 68
119					34 184.971 21	-0.000 44	34 164.268 29	0.001 44
120					34 185.100 88	0.001 86	34 164.397 20	0.001 48
121							34 164.522 73	0.001 43
122							34 164.644 41	0.000 98
123							34 164.763 99	0.000 98
124							34 164.880 45	0.000 86
125							34 164.994 08	0.000 71
<hr/>								
n	$(1, 7) \rightarrow np(1, 7)_8$		$(1, 11) \rightarrow np(1, 11)_{12}$		$(1, 13) \rightarrow np(1, 13)_{13}$		$(1, 13) \rightarrow np(1, 13)_{14}$	
	$\tilde{\nu}_{\text{obs}}$	Δ	$\tilde{\nu}_{\text{obs}}$	Δ	$\tilde{\nu}_{\text{obs}}$	Δ	$\tilde{\nu}_{\text{obs}}$	Δ
111					34 104.765 65	0.002 05	34 104.779 35	-0.000 78
112			34 127.912 23	-0.000 15	34 104.924 48	0.002 16	34 104.937 27	-0.000 85
113			34 128.065 87	-0.000 41	34 105.078 49	0.001 95	34 105.091 12	-0.000 83
114			34 128.215 83	-0.000 32	34 105.228 61	0.001 83	34 105.240 71	-0.001 04
115			34 128.362 28	0.000 14	34 105.375 10	0.001 84	34 105.387 23	-0.000 43
116			34 128.503 62	-0.000 75	34 105.516 80	0.001 35	34 105.528 97	-0.000 86
117	34 164.019 55	-0.001 82	34 128.643 33	0.000 35	34 105.655 89	0.001 37	34 105.667 53	-0.000 84
118	34 164.154 88	-0.001 18	34 128.778 05	-0.000 04	34 105.791 79	0.001 56	34 105.803 47	0.000 06
119	34 164.285 15	-0.002 24	34 128.909 62	-0.000 19	34 105.922 05	0.000 64	34 105.934 29	-0.000 78
120	34 164.414 68	-0.000 78	34 129.038 05	-0.000 21	34 106.050 97	0.000 68	34 106.063 12	-0.000 33
121	34 164.539 82	-0.000 57	34 129.163 37	-0.000 17	34 106.176 32	0.000 54	34 106.188 12	-0.000 55
122	34 164.661 43	-0.000 84	34 129.285 53	-0.000 22	34 106.299 89	0.001 04	34 106.310 91	0.000 09
123	34 164.780 40	-0.000 81	34 129.405 48	0.000 47	34 106.418 41	0.000 51	34 106.429 58	-0.000 44
124	34 164.896 30	-0.000 99	34 129.521 99	0.000 60	34 106.534 63	0.000 27	34 106.546 09	-0.000 25
125	34 165.009 78	-0.000 83	34 129.635 15	0.000 15				
126			34 129.745 99	0.000 08				
127			34 129.854 46	0.000 23				
128			34 129.960 27	0.000 26				
129			34 130.063 64	0.000 29				

V. DISCUSSION AND CONCLUSIONS

The differences between the term values that were determined experimentally in this work and the term values that were calculated *ab initio* are plotted as full squares in Fig. 3. For comparison, Fig. 3 also displays the differences between experimental [27] and theoretical [14] energies of rotational levels of the $v^+ = 0$ vibrational ground state of He_2^+ as open squares. The discrepancies between theoretical and experimental term values of rotational levels of the $v^+ = 0$ and 1 vibrational levels of He_2^+ behave similarly: Experimental term values are always larger than the calculated ones and the deviation increases rapidly with increasing rotational quantum number, reaching a value of almost 0.8 GHz for $v^+ = 1, N^+ = 13$.

A set of effective rotational constants was derived from the obtained rovibrational energies of He_2^+ and the results are summarized in Table IV. The T_1 term corre-

sponds to the rotationless fundamental vibration of He_2^+ and its value of $1628.3832(12) \text{ cm}^{-1}$ agrees with the *ab initio* prediction of Tung *et al.* of $1628.380(4) \text{ cm}^{-1}$ [14] within the combined experimental and theoretical uncertainty, but is about four times more precise.

Although the *ab initio* calculations are able to predict the rotationless fundamental vibration within the quoted uncertainty, the experimental rotational term values are not reproduced well by the calculations, the discrepancies increasing steadily with increasing rotational quantum number. A similar discrepancy between theory and experiment was observed for the rotational energies of the vibrational ground state of He_2^+ , supporting our previous conclusion that the approximate treatment of the nonadiabatic correction through R -independent reduced masses in Ref. [14] becomes increasingly inaccurate as N^+ increases [27] (see also Ref. [29]).

Table III. Estimated statistical (1σ) and systematic contributions to the uncertainty in the determinations of the absolute (abs.) transition wavenumbers (second column) and the relative (rel.) positions (third column) of the ionic levels obtained by building combination differences to obtain the rotational intervals of the $\text{He}_2^+ X^+ {}^2\Sigma_u^+$ ($v^+ = 1$) state. All values are given in MHz.

Source	$\sigma_{\text{abs.}}$	$\sigma_{\text{rel.}}$
<i>Statistical</i>		
Wavenumber calibration	25	25
Term values of He_2^*	20	20
Determination of line centers	5	5
MQDT fit	5-10	5-10
Total statistical	35	35
<i>Systematic</i>		
Wavenumber calibration	40	0
AC-Stark shift	2	0
DC-Stark shift	25	10
Zeeman shift	1	0
Doppler shift	5	0
Pressure shift	1	0
Total systematic	48	10

Table IV. Effective rotational constants of the $X^+ {}^2\Sigma_u^+$ ($v^+ = 0, 1$) state of He_2^+ derived from the rovibrational term values reported in Ref. [27] and Table I. All values are given in cm^{-1} .

	$v^+ = 0$	$v^+ = 1$
T_{v^+}	0	1628.3832(12)
B_{v^+}	7.101 140(25)	6.875 14(8)
$D_{v^+} \times 10^4$	5.2138(35)	5.211(11)
$H_{v^+} \times 10^8$	3.22(16)	2.83(38)
$L_{v^+} \times 10^{12}$	-6.5(22)	—

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