**Precision measurements in few-electron molecules:**
The ionization energy of metastable $^4\text{He}_2$ and the first rotational interval of $^4\text{He}_2^+$

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Molecular helium represents a benchmark system for testing *ab initio* calculations on few-electron molecules. We report on the determination of the adiabatic ionization energy of the $a^3\Sigma_u^+$ state of He$_2$, corresponding to the energy interval between the $a^3\Sigma_u^+$ ($v'' = 0, N'' = 1$) state of He$_2$ and the $X^+\Sigma_u^+$ ($v^+ = 0, N^+ = 1$) state of He$_2^+$, and of the lowest rotational interval of He$_2^+$. These measurements rely on the excitation of metastable He$_2$ molecules to high Rydberg states using frequency-comb-calibrated continuous-wave UV radiation in a counter-propagating-laser-beam setup. The observed Rydberg states were extrapolated to their series limit using multichannel quantum-defect theory. The ionization energy of He$_2$ ($a^3\Sigma_u^+$) and the lowest rotational interval of He$_2^+$ ($X^+\Sigma_u^+$) are $34301.207002(23)\pm 0.000037\text{ cm}^{-1}$ and $70.937589(23)\pm 0.000060\text{ cm}^{-1}$, respectively.

The comparison of the results of precision spectroscopic measurements in few-electron atoms and molecules with the results of *ab initio* calculations challenges theoreticians and experimentalists and forces them to constantly improve their respective methodologies. In recent years, this symbiotic relation between theory and experiment has opened a route to test the Standard Model of particle physics and extensions thereof [1–4] and to dramatically improve their respective methodologies. In recent years, this symbiotic relation between theory and experiment has opened a route to test the Standard Model of particle physics and extensions thereof [1–4] and to dramatically improve their respective methodologies.

The ionization energy of metastable He$_2$ in its vibronic ground state ($X^+\Sigma_u^+$) and weakly bound $A^+\Sigma_u^+$ levels of He$_2^+$ have been measured with a 1 MHz precision [16] but they are not sensitive to $\alpha_0$ either because the effects of the long-range interactions largely cancel out in the energy differences. Experimental data on a broader range of levels of He$_2^+$ are thus required.

We present the results of a determination of the adiabatic ionization energy of metastable He$_2$ in its $a^3\Sigma_u^+$ state (He$_2^*$ hereafter) and the first rotational interval of He$_2^+$ in its vibronic $X^+\Sigma_u^+$ ($v^+ = 0$) ground state (He$_2^+$ hereafter) at a relative accuracy of $10^{-9}$ and $8.5 \times 10^{-7}$, respectively. These results improve our previous results on this system by more than an order of magnitude [17, 18] and approach the level of accuracy required by the metrological application described above. They also serve as benchmark data for *ab initio* calculations of three- and four-electron systems [19, 20].

Our approach consists of measuring Rydberg series of He$_2$ from the metastable $a^3\Sigma_u^+$ state of He$_2$ and extrapolating them to the series limits. The two lowest rotational levels of He$_2^*$ and the np Rydberg series converging on the corresponding rotational levels of He$_2^+$ are schematically depicted in Fig. 1. Only odd rotational levels $N''$ and $N^+$ are allowed in He$_2^*$ and He$_2^+$, respectively, because $^4\text{He}_2^+$ is a boson. We use double-primed symbols, unprimed symbols, and a superscript “+” to designate the quantum numbers of He$_2^*$, He$_2$ Rydberg states, and He$_2^+$, respectively. The level structure of He$_2^*$ is adequately described using Hund’s angular-momentum coupling case (b), i.e., the total angular momentum excluding spin $\tilde{N}''$ couples to the total electron spin $\tilde{S}''$ to form the total angular momentum $\tilde{J}''$. The splittings between the resulting fine-structure components with $J'' = N''$, $N'' \pm 1$ are known very accurately from radio-frequency measurements [21, 22]. The level structure of He$_2^+$ is also best described using Hund’s angular-momentum coupling case.
The rotational levels of He₂⁺ are split into two spin-rotation components with \( J^+ = N^+ \pm \frac{1}{2} \) and the splittings for rotational states with \( N^+ \leq 27 \) were recently measured, with an accuracy of 150 kHz for \( N^+ = 1 \) [23].

Rydberg states of He₂ with principal quantum numbers \( n \lesssim 200 \) are well described in Hund’s case (d) coupling. The rotation of the ionic core excluding spin \( \vec{N}^+ \) couples to \( \vec{S} \) to give \( \vec{N} \), which couples to \( \vec{J} \) to give the total angular momentum of the Rydberg state \( \vec{J} \). The triplet \((S = 1)\) np Rydberg states of He₂ are split in nine fine-structure components [23]. For \( n \gtrsim 200 \), Hund’s coupling case (e[b]) applies, in which singlet and triplet states are mixed (See Ref. [23] for details). The energy-level structures resulting from these coupling schemes are schematically depicted on the right-hand side of Fig. 1.

Because the transition-dipole-moment operator does not act on spins, transitions from He₂⁺ to np Rydberg states are governed by the selection rule \( \Delta J = J - J'' = N - N'' = \Delta N \) [23]. The observed Rydberg-transition wavenumbers are extrapolated to their series limit using multichannel quantum-defect theory (MQDT) [24], yielding the adiabatic ionization energy of He₂⁺ and the first rotational interval of He₂⁺. The Rydberg transitions observed in our spectra connect the Hund’s case (b) levels of He₂⁺ to the Hund’s case (d) Rydberg levels and can be labeled as \( N''p \rightarrow npN''_{N,J} \). Here we also report fine-structure-free values for the transition wavenumbers, in which case the subscript labels \( J'' \) and \( J \) are omitted.

![Figure 1. Energy-level diagram (not to scale) showing the lowest rovibrational states of He₂⁺ and np Rydberg series converging on the corresponding rovibrational states of He⁺.](image)

The measurements were carried out using the experimental apparatus described in Ref. [23], specifically adapted to (i) record first-order-Doppler-corrected single-photon transitions [25–27] and (ii) calibrate the transition frequencies using a frequency comb [28].

Pulsed supersonic beams of He₂⁺ molecules are produced in a discharge of pure helium [29]. Beam velocities of about 1000 m/s and 500 m/s are obtained by cooling the valve body to 77 K and 10 K, respectively [30]. A 3-mm skimmer selects the most intense part of the molecular beam, which intersects the laser radiation at near right angles after about 1 m of free flight. Transitions to Rydberg states with \( n \gtrsim 30 \) are detected by applying a pulsed electric field of 750 V/cm across a cylindrically symmetric stack of electrodes. The pulsed ionization field also serves to accelerate the produced He₂⁺ ions toward an off-axis microchannel-plate (MCP) detector. A spectrum is recorded by monitoring the ion yield as a function of the laser frequency.

The narrow-bandwidth \(< 1 \text{ MHz}\) UV radiation used for the excitation of He₂⁺ to np Rydberg states is produced by frequency doubling the output of a cw ring dye laser tunable around 580 nm with a beta-barium borate (BBO) crystal mounted in a feedback-stabilized external cavity. The Doppler-corrected transition frequencies are measured by retroreflecting the laser beam after it passes the interaction zone, thereby generating two Doppler-shifted components in the spectrum. Their geometric mean corresponds to the first-order-Doppler-free transition frequency in case of a perfect overlap between the two counter-propagating beams. Care was taken to minimize the waist of the laser beam, by means of a telescope, at the position corresponding to the surface of the backreflecting mirror, which was used to overlap the forward- and backward-propagating beams over a path length of about 10 m. The systematic uncertainty associated with the difficulty of achieving a perfect overlap of the two beams (see Ref. [25] for details) effectively transformed into a statistical uncertainty of 460 kHz when repeating the measurements multiple times after complete realignment of the laser beams.

Absolute calibration of the fundamental laser frequency relies on the use of an optical frequency comb (Menlo Systems FC1500-250-ULN), referenced to a GPS-disciplined Rb oscillator. The Rb oscillator (Stanford Research Systems FS725) has a stability of \( 2 \times 10^{-11} \) over the time \( (1 \text{s}) \) required to record one data point and the GPS receiver (Spectrum Instruments TM-4) has a specified long-term stability of \( 10^{-12} \) [28]. The beat signal measured with the photodiode is filtered by the frequency-comb electronics and is compared with a passive frequency discriminator inside a home-built electronic unit to generate an error signal, as described in Ref. [31]. This signal is used to control the reference cavity of the laser [31] and to ensure, by means of a proportional-integral-derivative (PID) feedback-controlled loop, that the beat frequency is locked at 60 MHz [32]. The frequency of the laser follows from \( f_L = n_c f_e \pm 2f_{CEO} \pm f_{\text{beat}} \), where \( f_{CEO} \) and \( f_e \) are
the carrier-envelope-offset and repetition frequency of the frequency comb, respectively, and \( n_e \) is the mode number that generates the beat signal, as determined using a wavemeter.

A small dc electric potential is applied to the stack to compensate the stray electric field along the symmetry axis. Four pin electrodes are employed to compensate the stray field in the plane perpendicular to the symmetry axis, resulting in an overall field compensation of better than 1 mG [18], corresponding to a measured frequency shift of less than 200 kHz for Rydberg states of \( n \approx 100 \). The interaction region is enclosed in two concentric mumetal shields to suppress stray magnetic fields ≈ frequency shift of less than 200 kHz for Rydberg states of \( n \approx 100 \). The interaction region is enclosed in two concentric mumetal shields to suppress stray magnetic fields.

![Figure 2](image)

Figure 2. Upper panel: Experimental data (black dots) and weighted-fit model (red curve) of transitions to Rydberg states. The symbol ∆ = (obs. − calc.) represents the difference between observed and calculated line positions. All values are given in cm⁻¹.

| \( n \) | \( \tilde{\nu}_{\text{obs}} (\sigma_{\tilde{\nu}_{\text{obs}}}) \) | \( \Delta \times 10^6 \) | \( \tilde{\nu}_{\text{obs}} (\sigma_{\tilde{\nu}_{\text{obs}}}) \) | \( \Delta \times 10^6 \) |
|---|---|---|---|---|
| 70 | 34.285.974.192(9) | -12 | 34.288.048.567(12) | 14 |
| 115 | 34.288.024.156(9) | -11 | 34.288.278.429(10) | 29 |
| 117 | 34.288.305.868(9) | -23 | 34.288.327.945(10) | 29 |
| 121 | 34.288.827.917(12) | -32 | 34.288.846.249(10) | 48 |

| \( n \) | \( \tilde{\nu}_{\text{obs}} (\sigma_{\tilde{\nu}_{\text{obs}}}) \) | \( \Delta \times 10^6 \) | \( \tilde{\nu}_{\text{obs}} (\sigma_{\tilde{\nu}_{\text{obs}}}) \) | \( \Delta \times 10^6 \) |
|---|---|---|---|---|
| 3428.945(10) | -10 | 3428.846.249(10) | 48 |

Table I. Observed transitions from the \( a^3\Sigma_u^+ (\nu'' = 0, N'' = 1, 3) \) state of \( ^4 \)He\( _2 \) to the np\( v_2 \) \( N \) Rydberg states belonging to series converging to the \( X^+ \) \( a^3\Pi_u \) (\( \nu' = 0, N' = 1, 3 \) states of \( ^4 \)He\( _2 \)" and comparison with the results of MQDT calculations. The symbol \( \Delta = (\text{obs.} - \text{calc.}) \) represents the difference between observed and calculated line positions. All values are given in cm⁻¹.

![Diagram](image)

Fig. 3 illustrates the \( 1_s \rightarrow 81p_{12} \) transition recorded at valve temperatures of 77 K (red) and 10 K (blue). The two spectra clearly demonstrate the reduction of the Doppler width and Doppler shift associated with imperfect alignment of the laser and molecular beams. This asymmetry can be reduced by lowering the velocity of the molecular beam and/or improving the laser wavefront, but it does not affect the Doppler-corrected line positions because the two lines of the Doppler pair
Figure 3. Comparison of the fitted $1 \rightarrow 81p^1_2$, Rydberg spectra recorded at 77 K (red trace) and 10 K (blue trace), resulting in a FWHM of 21 MHz and 11 MHz, respectively. The spectra are normalized to their respective maximum intensity, which is reduced by a factor of four when cooling the valve to 10 K. The insert shows the determined Doppler-corrected transition frequencies on a magnified scale. See text for details.

display an opposite asymmetry.

The extrapolation to the series limit relies on MQDT as developed and implemented by Ch. Jungen [24, 34, 35]. The MQDT parameters of triplet $np$ and $nf$ Rydberg states determined by Sprecher et al. [36] were employed without change. In order to ensure the robust extrapolation of ionization energies, we adopt the approach of Beyer et al. [37]. The experimental data set used for the extrapolation is chosen so as to cover an energy range at least as large as the energy interval to be extrapolated. The extrapolated ionization energy of the $N'' = 1$ rotational level of He$_2^+$ amounts to $\tilde{\nu}_{11} = 34301.207002(23)$ cm$^{-1}$. The comparison between the centers of gravity of the observed transitions and calculated values resulting from the MQDT fit are also shown in Table I. The root mean square (RMS) of the discrepancies amounts to 740 kHz and the residuals appear to be normally distributed.

The data also allow the determination of the first rotational interval of He$_2^+$, provided the rotational energy corresponding to the $N'' = 1 \rightarrow N'' = 3$ transition in He$_2^+$ is known with sufficient accuracy. We determined this value to be $\tilde{\nu}_{13} = 75.812953(20)$ cm$^{-1}$ by taking the difference of the $1 \rightarrow 111p_{12}$ [34292.2596(17) cm$^{-1}$] and $3 \rightarrow 111p_{12}$ [34216.446617(10) cm$^{-1}$] transition wavenumbers. We find that the interval between the first two rotational states of He$_2^+$ is $\tilde{\nu}_{13} = 70.937589(23)$ cm$^{-1}$.

The estimated statistical and systematic uncertainties affecting the recorded transition frequencies are summarized in Table II. The dominant contribution to the systematic uncertainty comes from the MQDT extrapolation. In future this value might be reduced by improving the quantum defects of Ref. [36], which will require accurate measurements at principal quantum numbers $n$ in the range 20–40. The largest remaining contributions to the uncertainty are the uncertainty in the lineshape model, which corresponds to $\sim$1/20 of the linewidth, the residual dc-Stark shift and the uncertainty in the first-order Doppler shift. The latter is estimated from the day-to-day reproducibility of the $1_1 \rightarrow 97p_{12}$ transition frequency after realignment of the laser beams through the chamber (see Fig. 4). These measurements were also

![figure](image-url)

Figure 4. Statistical analysis performed on the $1_1 \rightarrow 97p_{12}$ transition ($f_{\text{mean}}/c = 34289.587861(23)$ cm$^{-1}$). The figure shows the difference $\Delta f = f - f_{\text{mean}}$ between the transition frequency recorded on different days with the average value $f_{\text{mean}}$ of all measurements. The different markers (triangles, squares and diamonds) denote different data sets after subsequent realignment procedures. The grey-shaded areas include the data points within one and two standard deviations, respectively ($1\sigma = 700$ kHz).

Table II. Systematic and statistical ($1\sigma$, in kHz) contributions to the uncertainty in the determination of the ionization potential $\tilde{\nu}_{11}$ of He$_2^+$ (third column) and in the lowest rotational interval $\tilde{\nu}_{13}$ of He$_2^+$ (second column). All systematic uncertainties with the exception of the MQDT-extrapolation uncertainty cancel out in the determination of the rotational interval.

| Uncertainty (kHz) | $\tilde{\nu}_{13}$ | $\tilde{\nu}_{11}$ |
|-------------------|------------------|------------------|
| **Systematic**     |                  |                  |
| ac-Stark shift     | $\ll 1$          |                  |
| photon-recoil shift| $\ll 1$          |                  |
| second-order Doppler shift | $< 1$      |                  |
| pressure shift     | 5                |                  |
| Zeeman shift       | 10               |                  |
| dc-Stark shift     | 200              |                  |
| MQDT extrapolation | 1700             | 1100             |
| **Statistical**    | 700              | 700              |

$^a$ Including the contribution of the residual first-order Doppler shift ($\sim$460 kHz) and the lineshape model ($\sim$400 kHz) (see text).
used to estimate the overall statistical reproducibility to 700 kHz. The recoil shift and the second-order Doppler shift amount to 50 kHz and -5 kHz, respectively, and were compensated when deriving the final transition frequencies. The remaining contributions to the error budget were too small to be quantified in our experiment and have been estimated.

We improved the uncertainty of the adiabatic ionization energy of the \( a^3\Sigma^+_u \) state of \( \text{He}_2 \) (1.3 MHz) and the first rotational interval of \( \text{He}_2^+ \) (1.9 MHz) by a factor of 30 and 10, respectively, compared to our previous studies (see Table III). This improvement was achieved by replacing the pulsed UV laser used for photoexcitation by a single-mode cw UV laser and by calibrating the laser frequency with a frequency comb rather than a commercial wavemeter. Our measurements provide benchmark data to complement the current most accurate results that rely on dielectric-constant gas thermometry [38].

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Table III. Comparison of the adiabatic ionization energy of \( \text{He}_2^+ \) (\( \tilde{\nu}_{11} \)) and of the lowest rotational interval of \( \text{He}_2^+ \) (\( \tilde{\nu}_{13} \)) and of \( \text{He}_2^+ \) (\( \tilde{\nu}_{13} \)) obtained in this work and in previous studies. All values are given in cm\(^{-1}\).

| Reference | \( \tilde{\nu}_{11} \) | \( \tilde{\nu}_{13} \) | \( \tilde{\nu}_{13} \) |
|-----------|----------------|----------------|----------------|
| Ref. [39] | 34.301.22(10) | 70.99(14) | 70.99(14) |
| Ref. [40] | 34.301.2(3) | 75.8129(3) | 70.936 |
| Ref. [29] | 34.301.211(10) | 70.937(3) | 70.937(3) |
| Ref. [17] | 34.301.2059(14) | 75.8137(4) | 70.9380(6) |
| Ref. [20] | 34.301.2070(00) | 75.812953(20) | 70.93759(6) |

* Containing an estimated value of the relativistic and QED corrections. The nonadiabatic term value is 70.936 cm\(^{-1}\) [20].

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