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# High-resolution leak-out spectroscopy of $\text{HHe}_2^+$

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Applying a novel and universal action spectroscopic technique, called leak-out spectroscopy, this paper revisits the  $\nu_3$  proton shuttle motion of the symmetric linear molecule  $\text{He-H}^+-\text{He}$ . For this, a 4 K cryogenic ion trap apparatus has been combined with a high-resolution quantum cascade laser operating around  $1300\text{ cm}^{-1}$ . Seven rovibrational lines of this fundamental three-nucleus-four-electron system are recorded, demonstrating the suitability of the leak-out method for such fundamental hydrogen–helium cations.

## 1. Introduction

A proton solvated by helium atoms,  $\text{HHe}_n^+$ , is an interesting molecular system. The first ion in this series, the  $\text{H}_2$ -like and strongly bound  $\text{HHe}^+$  cation, has been known in the laboratory since 1925,<sup>1</sup> has been investigated by high-resolution spectroscopy,<sup>2–7</sup> and was detected in space quite recently.<sup>8</sup> The next ion within this series,  $\text{He-H}^+-\text{He}$  (ref. 9–16), is a linear three-nucleus-four-electron system. It is fairly strongly bound with a dissociation energy of  $D_0 = 3931 \pm 20\text{ cm}^{-1}$  (ref. 14), whereas all additional He atoms in higher order complexes ( $n = 3–6$ ) are loosely bound to the central proton by less than  $200\text{ cm}^{-1}$ . The species  $n = 3–6$  have been investigated by low resolution vibrational predissociation spectroscopy,<sup>17</sup> in which the anti-symmetric stretch ( $\nu_3$ ) and bend ( $\nu_2$ ) fundamentals of the  $\text{He-H}^+-\text{He}$  core were observed around  $1300\text{ cm}^{-1}$  and  $850\text{ cm}^{-1}$ , respectively. More recently, the  $\nu_3$  mode of “naked”  $\text{He-H}^+-\text{He}$  has been investigated in high resolution, with three rovibrational lines detected.<sup>18</sup> This particular mode,  $\nu_3$ , is the proton shuttle motion and can be considered as a molecular realization of a Hertzian dipole, with its infrared (IR) intensity computed harmonically to be as large as  $2661\text{ km mol}^{-1}$ .<sup>13</sup>

The invention of the leak-out-spectroscopy method (LOS<sup>19</sup>) has boosted ion-trap-based spectroscopy of molecular ions, as it is a universal and close to background-free technique, with many recent applications to astrophysically relevant

cations.<sup>19–27</sup> In brief, LOS exploits the fact that the vibrational energy of a laser-excited ion can be converted into kinetic energy in a collision with a suitable neutral molecule or atom. These accelerated ions may then escape the ion trap and can be counted in a detector. By counting the “leaked-out” ions as a function of the laser wavelength, a spectrum is generated. In the current work, we revisit the  $\nu_3$  mode of  $\text{He-H}^+-\text{He}$  with the LOS method, using the very He atoms in the ion trap as the neutral collision partner required for LOS. The high-quality results obtained for  $\text{HHe}_2^+$  encourage us to investigate further fundamental hydrogen–helium cations with LOS.

## 2. Experimental methods

The experiments of this study have been carried out in the cryogenic 22-pole ion trapping instrument COLTRAP.<sup>28</sup> In brief, a pulse of several ten thousand  $\text{HHe}^+$  ions was generated in an ion source by electron impact ionization of an  $\text{H}_2$ –He mixture, selected in a quadrupole mass spectrometer for a mass range 2–6 u (exact selection was considered not necessary), and then injected into the 22-pole trap.<sup>29</sup> The trap was held at a temperature of  $T = 4\text{ K}$  and was constantly filled with He gas ( $\sim 10^{15}\text{ cm}^{-3}$ ). During the trapping time of typically several 100 ms, the cold He gas fulfilled two roles: primarily, it enabled  $\text{HHe}_2^+$  ions to be formed by 3-body collisions, and secondarily, it served as the collision partner required for the leak-out of the  $\text{HHe}_2^+$  ions. For LOS, the ion ensemble was irradiated with narrow-bandwidth  $7.5\text{ }\mu\text{m}$  IR radiation, which passed through the ion trap with a measured power on the order of 40 mW. The ions leaking out from the trap during the trapping time were selected in a second quadrupole for mass 9 u, and counted in a high-efficiency ion counter. The light source was a quantum

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cascade laser (Daylight Solutions) operating in the range of 1284–1355  $\text{cm}^{-1}$ , whose frequency was measured by a wave-meter (Bristol model 621 A-XIR).

### 3. Results and discussion

The high resolution LOS spectrum obtained for the proton-shuttle motion  $\nu_3$  of  $\text{HHe}_2^+$  is shown in Fig. 1. Similar to  $\text{CO}_2$ , only levels with even rotational quantum number  $J$  are allowed in the ground state owing to nuclear spin statistics. An analysis of the observed line widths ( $\sim 60$  MHz including an estimated laser linewidth of  $\sim 30$  MHz) yields a kinetic temperature of about  $T_{\text{kin}} \approx 30$  K, and the simulation of the intensity distribution seen in Fig. 1, obtained with PGOPHER,<sup>30</sup> corresponds to a

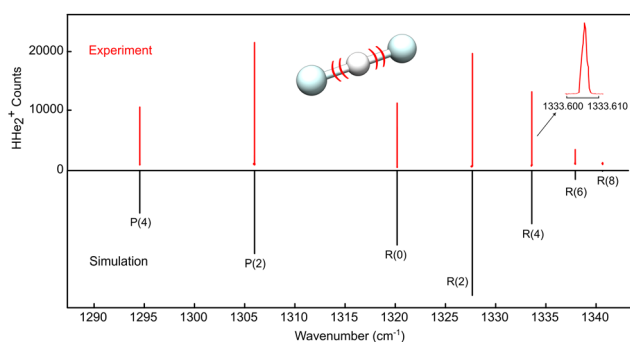


Fig. 1 LOS spectrum of the  $\nu_3$  antisymmetric stretching band of  $\text{HHe}_2^+$ . The upper part shows the experimental spectrum, obtained by individually targeting the transitions, as shown for the zoom of the line  $R(4)$ . The lower part is a stick spectrum simulated at a temperature of 35 K using the fitted parameters from Table 2.

Table 1 Experimental and first-principles computed rovibrational transitions of  $\text{HHe}_2^+$  (in  $\text{cm}^{-1}$ )

	$(\nu_3, J')$	$\leftarrow$	$(\nu_3, J'')$	Experiment	First principles
$P(4)$	(1,3)	$\leftarrow$	(0,4)	1294.5488(4)	1294.28
$P(2)$	(1,1)	$\leftarrow$	(0,2)	1305.9777(4)	1305.72
$R(0)$	(1,1)	$\leftarrow$	(0,0)	1320.1882(4)	1319.93
$R(2)$	(1,3)	$\leftarrow$	(0,2)	1327.6915(4)	1327.43
$R(4)$	(1,5)	$\leftarrow$	(0,4)	1333.6069(4)	1333.35
$R(6)$	(1,7)	$\leftarrow$	(0,6)	1337.9292(4)	1337.67
$R(8)$	(1,9)	$\leftarrow$	(0,8)	1340.6515(4)	1340.39

Table 2 Spectroscopic parameters of  $\text{HHe}_2^+$  (in  $\text{cm}^{-1}$ ), obtained by fitting the data given in Table 1 with the PGOPHER<sup>30</sup> program, along with previously reported computational results<sup>13,15,18</sup>

	This work		First principles		<i>Ab initio</i> , ref. 18		<i>Ab initio</i> , ref. 13		<i>Ab initio</i> , ref. 15
	Experimental		First principles		<i>Ab initio</i> , ref. 18		<i>Ab initio</i> , ref. 13		<i>Ab initio</i> , ref. 15
	$\nu_3 = 0$	$\nu_3 = 1$	$\nu_3 = 0$	$\nu_3 = 1$	$\nu_3 = 0$	$\nu_3 = 1$	$\nu_3 = 0$	$\nu_3 = 1$	$\nu_3 = 1$
$\nu_3$		1315.8444(2)		1315.58		1306.2		1345.2	1318.6
$B$	2.36877(6)	2.17208(6)	2.3693	2.1726	2.3616	2.1491	2.3622	2.1506	
$D$	0.000056(2)	0.000052(2)	0.00005	0.00005	0.000046		0.00004		

rotational temperature of  $T_{\text{rot}} = 35$  K. While much lower temperatures could be obtained by optimizing some experimental settings (*e.g.* by better mass selection and storing less ions), the high temperature of the spectrum shown in Fig. 1 serendipitously permitted us to record as many as seven rovibrational lines, given in Table 1. The lines show excellent agreement, with a difference of only  $0.26 \text{ cm}^{-1}$ , with accurate variationally calculated values (“first principles”, also listed in Table 1), obtained with the same methodology as used in ref. 16. This constant difference is solely due to the vibrational contribution, whereas the rotational structure in the ground and vibrationally excited states is matched extremely well. Performing a least-squares fit of the observed lines using a linear rotor Hamiltonian as implemented in PGOPHER, the spectroscopic parameters shown in Table 2 are obtained. As can be seen in Table 2, there is a large change of the rotational constant  $B$  upon vibrational excitation whose value decreases by about 10% in comparison to the ground state. This difference is caused by the shallow and anharmonic potential energy surface of  $\text{HHe}_2^+$  that results in the asymmetric appearance of the  $\nu_3$  band depicted in Fig. 1.

### 4. Conclusion and outlook

In conclusion, the exceptional sensitivity of LOS and its application to the  $\nu_3$  proton shuttle motion of  $\text{HHe}_2^+$  allowed us to detect seven of its rovibrational lines, four of which are reported here for the first time. In comparison to our former work,<sup>18</sup> a much better determination of the spectroscopic parameters of  $\text{HHe}_2^+$  (see Table 2) could be achieved here. Our novel results will certainly facilitate astronomical searches for  $\text{HHe}_2^+$ , preferentially in the infrared region using the recently launched James Webb Space Telescope. After this successful demonstration, we plan to measure the bending mode  $\nu_2$  or the combination band  $\nu_1 + \nu_3$  of  $\text{HHe}_2^+$ , with calculated band origins of  $\nu_2 = 874.9 \text{ cm}^{-1}$  and  $\nu_1 + \nu_3 = 2057.9 \text{ cm}^{-1}$  (ref. 16), respectively. An equally attractive target is the fundamental  $\text{H}_2$  stretch in linear  $\text{H}_2\text{He}^+$ , or the  $\text{D}_2$  stretch in  $\text{D}_2\text{He}^+$ . The wavenumber of the latter is predicted to be at  $1318 \text{ cm}^{-1}$  (ref. 31), which we could confirm by recording its first rovibrational fingerprints, using the same quantum cascade laser as in this work.



## Data availability

All the important data (transition frequencies) are contained in Table 1.

## Conflicts of interest

There are no conflicts to declare.

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