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Spectroscopic signatures of HHe₂⁺ and HHe₃⁺†

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Using two different action spectroscopic techniques, a high-resolution quantum cascade laser operating around 1300 cm⁻¹ and a cryogenic ion trap machine, the proton shuttle motion of the cations HHe₂⁺ and HHe₃⁺ has been probed at a nominal temperature of 4 K. For HHe₃⁺, the loosely bound character of this complex allowed predissociation spectroscopy to be used, and the observed broad features point to a lifetime of a few ps in the vibrationally excited state. For He–H⁺–He, a fundamental linear molecule consisting of only three nuclei and four electrons, the method of laser-induced inhibition of complex growth (LIICG) enabled the measurement of three accurate rovibrational transitions, pinning down its molecular parameters for the first time.

Species of the type HHe$_n^+$ are composed of the two most abundant elements of the universe. The first ion in this series, the strongly bound HHe⁺ cation, which is thought to be the very first diatomic formed when the early universe cooled down,[1] is known in the laboratory since 1925[2] and has been investigated by high-resolution vibrational[3–6] and rotational[7,8] spectroscopy. Enabled by the latter, the detection of HHe⁺ in interstellar space was achieved recently, *via* the GREAT receiver on-board the SOFIA airplane.[9]

Based on mass spectrometry studies[10–13] and high-level first-principles quantum-chemical computations,[12,14,15] the larger HHe$_n^+$ species (n = 2–6) are known to consist of a relatively strongly bound He–H⁺–He core, with a dissociation energy of D_0 = 3931 ± 20 cm⁻¹ (ref. 12), while additional He atoms are loosely bound to the central proton by only about 200 cm⁻¹. A review about these and other cationic noble gas hydrides can be found in ref. 16. Recently, the species n = 3–6 have been

investigated by low resolution vibrational predissociation spectroscopy,[17] locating the asymmetric stretch (ν_3) and bend (ν_2) fundamentals of the He–H⁺–He core to be around 1300 cm⁻¹ and 850 cm⁻¹, respectively. Based on this information, we have investigated the ν_3-like asymmetric stretch motion of the n = 2–6 cations in high resolution. The very short (∼ps) lifetime and the associated line broadening of the predissociation states precludes resolution of single rovibrational lines for the cases n = 3–6, whereas for n = 2 the longevity of the ν_3 = 1 state enables the detection of very narrow rovibrational lines at a temperature of 4 K, which in turn yield molecular parameters for this fundamental three-nucleus-four-electron system for the first time.

The experiments of this study have been carried out in the cryogenic 22-pole ion trapping instrument COLTRAP.[18] In brief, a pulse of tens of thousands of HHe⁺ ions was generated in an ion source by electron impact of a H₂–He mixture, selected in a quadrupole mass spectrometer for mass 5 u, and then injected into the cryogenic 22-pole ion trap.[19] The trap was held at a temperature of T = 4 K and was filled with He in a constant or pulsed fashion (∼10¹⁵ cm⁻³). During the trapping time of typically 800 ms, the cold HHe$_n^+$ ion ensemble formed by 3-body collisions was continuously irradiated with narrow-bandwidth 7.5 μm infrared (IR) radiation, passing through the ion trapping machine *via* two CaF₂ Brewster window assemblies,[20] and with power on the order of 180 mW. After the trapping period, the trap content was extracted, selected in a second quadrupole for a specific mass, and counted in a high-efficiency ion counter. The light source was a quantum cascade laser (Daylight Solutions) operating in the range of 1284–1355 cm⁻¹. The laser frequency was measured by a wavemeter (Bristol model 621 A-XIR), which was additionally calibrated with N₂O lines[21] during the high-resolution HHe₂⁺ measurements.

The experiments are complemented by high-level quantum-chemical calculations. Full configuration interaction (FCI) computations, equivalent to CCSDTQ (coupled cluster with single, double, triple, and quadruple excitations), can be executed straightforwardly for the four-electron HHe₂⁺ system. Similar CCSDTQ computations were carried out for HHe₃⁺. The *ab initio*

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† Electronic supplementary information (ESI) available: Summary of the spectra for HHe₃⁺ through HHe₆⁺. See DOI: 10.1039/d0cp04649c

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Phys. Chem. Chem. Phys., 2020, **22**, 22885–22888 | **22885**

Table 1 Spectroscopic parameters of HHe_2^+ and HHe_3^+ (in cm^{-1})

		Experimental		Ab initio[b]		Ref. 15	
		$\nu_3 = 0$	$\nu_3 = 1$	$\nu_3 = 0$	$\nu_3 = 1$	$\nu_3 = 0$	$\nu_3 = 1$
HHe_2^+	ν_3		1315.8446[a]		1306.2		1345.2
	ω_e				1554.3		1549.3
	B	2.3687	2.1720	2.3616	2.1491	2.3622	2.1506
	D	0.000046[c]	0.000046[c]	0.000046		0.00004	
HHe_3^+	ν_3		1300.1(1)		—[d]		
	ω_e				1554.6		
	A	2.4	2.0	2.46[2.43]	[2.22]		
	B	1.1	1.0	1.30[1.17]	[1.20]		
	C	0.8	0.7	0.85[0.78]	[0.75]		

[a] Values for HHe_2^+ are obtained by fitting the data given in Table 2 with the program PGOPHER.[24] Due to the limited dataset, no uncertainties are given. [b] The *ab initio* results for HHe_2^+ and HHe_3^+ were obtained at the CCSDTQ level with the aug-cc-pVQZ and aug-cc-pVTZ basis sets, respectively, except those in brackets, obtained at the aug-cc-pVTZ CCSD(T) level. [c] The quartic centrifugal distortion constant D is fixed to the *ab initio* value. [d] No *ab initio* estimate is given due to the fluxional character of the ion.

results are collected in Table 1, and were obtained with the aug-cc-pVQZ and the aug-cc-pVTZ basis sets[22] for HHe_2^+ and HHe_3^+, respectively. The electronic-structure computations utilized the CFOUR code.[23]

To obtain the spectral features of HHe_2^+ shown in Fig. 1, we exploit the fact that excitation of this strongly bound cation can inhibit He-attachment in a ternary collision process at 4 K. Such a scheme was demonstrated first for electronic excitation[25] and later for rovibrational excitation[18,26] of a molecular cation, and is now referred to as LIICG (Laser Induced Inhibition of Complex Growth). The LIICG lines of HHe_2^+ are detected as narrow Gaussian dips in the HHe_3^+ counts (see Fig. 1). Due to the low temperature, and missing rotational states (similar to CO_2, only levels with even rotational quantum number J are allowed in the ground state owing to nuclear spin statistics), only three rovibrational lines, $P(2)$, $R(0)$, and $R(2)$ could be measured. An analysis of their
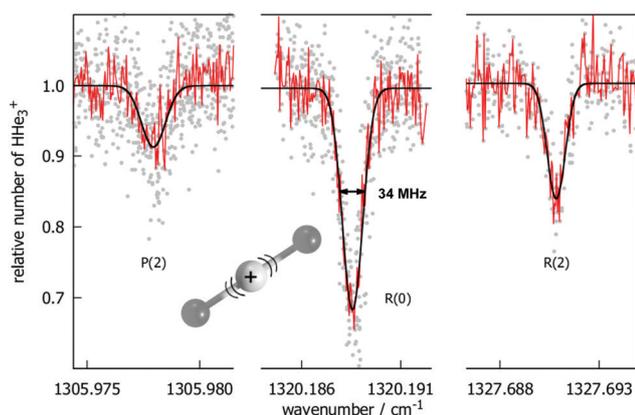
Fig. 1 Three LIICG (Laser Induced Inhibition of Complex Growth) lines from the ν_3 asymmetric stretching band of HHe_2^+. The measured data (grey) are normalized to the off-resonant HHe_3^+ counts ($\sim$1000), binned in 5×10^{-5} cm^{-1} steps (red), and fitted with a Gaussian line-shape (black), giving a FWHM (full width at half maximum) linewidth of 34 MHz.

observed width ($\sim$34 MHz including an estimated laser line-width of $\sim$10 MHz, as well as power broadening of $\sim$2 MHz) yields a kinetic temperature of $T_{kin} = 11$ K. The analysis of the intensity distribution seen in Fig. 1 and the failure to detect $R(4)$ result in a rotational temperature of $T_{rot} = 9.8(8)$ K. The accurate line positions are given in Table 2 and the retrieved spectroscopic parameters in Table 1. As seen there, the experimental and *ab initio* values for the rotational constants B of HHe_2^+ are in very good agreement, yielding for the first time a reliable experimental value for the proton-helium equilibrium bond length, $r_e^{expt.} = 0.924$ Å, obtained after correcting the measured B_0 to its equilibrium value B_e at the aug-cc-pVQZ FCI level.

As to HHe_3^+, the vibrational energy of the ν_3 fundamental exceeds the binding energy of the additional He atom, so that vibrational predissociation[27] takes place. Counting the number of this complex as a function of the laser frequency (in fact, the spectroscopic signals for both HHe_2^+ and HHe_3^+ are detected in the same mass channel), its vibrational excitation is detected as wide Lorentzian dips in the counts. The (inverted) predissociation signal obtained this way is depicted in Fig. 2. Due to the very short lifetime of the upper $\nu_3 = 1$ state, the broadening of all rovibrational transitions leads to wide, unresolved features. Because of this, and the very floppy nature of the additional He atom, a spectroscopic simulation with the program PGOPHER[24] turned out to be difficult; it yields a lifetime on the order of 4 ps, a band origin at 1300.1(1) cm^{-1}, and tentative rotational constants as given in Table 1. The short lifetime can be rationalized by the lost He atom being directly bound to the oscillating proton (besides the few degrees of freedom for this system). Second-order vibrational perturbation theory (VPT2) estimates of the anharmonic ν_3 fundamental are around 1330 cm^{-1}, with a corresponding harmonic value of 1555 cm^{-1} at the aug-cc-pVTZ CCSDTQ level. The considerable discrepancy from the measured value of 1300 cm^{-1} appears to be due to challenges resulting from the floppiness of HHe_3^+ adversely affecting the VPT2 treatment. Nonetheless, electronic-structure computations, at the aug-cc-pVTZ CCSDTQ level, yield a number of spectroscopic parameters for HHe_3^+, whose equilibrium structure is predicted to have C_{2v} point group symmetry. The short and long H$^+$–He equilibrium distances are 0.926 and 2.146 Å, respectively, while the rotational constants and the harmonic frequency ω_e are given in Table 1. The mentioned difficulty in simulating the spectrum is most probably not caused by splittings due to the exchange of the solvating outer He atom with one of the He atoms of the He–H$^+$–He core. This exchange is hindered by a transition state of C_{2v} point-group symmetry and a

Table 2 Measured rovibrational transitions[a] of HHe_2^+

	$(\nu_3, J') \leftarrow (\nu_3, J'')$	
$P(2)$	$(1,1) \leftarrow (0,2)$	1305.97768(7) cm^{-1}
$R(0)$	$(1,1) \leftarrow (0,0)$	1320.18837(7) cm^{-1}
$R(2)$	$(1,3) \leftarrow (0,2)$	1327.69123(7) cm^{-1}

[a] The precision of our cryogenic measurements is on the order of 0.4 MHz, but the accuracy is limited by calibration uncertainties to about 2 MHz.

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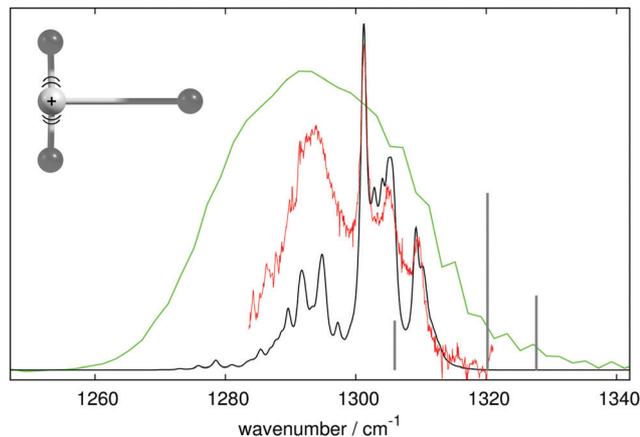
Fig. 2 The ν_3 asymmetric stretching band of HHe_3^+, measured at 4 K trap temperature (red trace). The short lifetime of the predissociating v_3 = 1 state leads to severe broadening (green trace: data from ref. 17, black trace: PGOPHER simulation, grey sticks: positions of HHe_2^+ lines from Fig. 1).

substantial electronic barrier height of about 1575 cm^{-1} (obtained at the aug-cc-pVQZ MP2 level).

In conclusion, our experimental benchmark values for HHe_2^+ facilitate the first astronomical search for this molecule in the IR. To eliminate the discrepancy between experiment and theory for this benchmark, one needs an accurate potential energy surface for HHe_2^+ as well as for HHe_3^+, so that variational rovibrational computations with an exact kinetic energy operator can be performed. Experimentally, we plan to measure the out-of-plane bending of HHe_3^+ located at about 888 cm^{-1}, which appears to be less affected by lifetime broadening.[17] In case of successful rovibrational resolution, and applying a rotational-rovibrational double resonance technique,[28] even highly resolved rotational spectroscopy of HHe_3^+ seems to be in reach. Also, using very similar techniques as described in this work, the fundamental rotational transitions of $HeHNe^+$ or $^3HeHHe^+$ (ref. 15) will be measured.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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