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Communication: High precision sub-Doppler infrared spectroscopy of the HeH⁺ ion

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The hydrohelium cation, HeH⁺, serves as an important benchmark for *ab initio* calculations that take into account non-adiabatic, relativistic, and quantum electrodynamic effects. Such calculations are capable of predicting molecular transitions to an accuracy of ~ 300 MHz or less. However, in order to continue to push the boundaries on these calculations, new measurements of these transitions are required. Here we measure seven rovibrational transitions in the fundamental vibrational band to a precision of ~ 1 MHz using the technique of Noise Immune Cavity Enhanced Optical Heterodyne Velocity Modulation Spectroscopy. These newly measured transitions are included in a fit to the rotation-vibration term values to derive refined spectroscopic constants in the $v = 0$ and $v = 1$ vibrational states, as well as to calculate rotation-vibration energy levels with high precision.

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I. INTRODUCTION

Composed of the two most abundant elements in the universe, the HeH⁺ cation is predicted to be among the first molecules ever formed,^{1,2} which makes this species of vital significance to chemical models of the early universe. Astronomical observations targeted at HeH⁺ have yet to yield an unequivocal detection of this molecule. The difficulty in detecting this species is attributed to the many chemical processes that compete with the formation of HeH⁺, ultimately resulting in a low abundance of this molecule. However, this molecule is easily formed in laboratory plasmas, which has spurred much experimental work on this fundamental species.

First discovered in 1925,³ the HeH⁺ ion has been the subject of many spectroscopic studies. In 1979, the first rovibrational spectrum of this molecule was acquired by Tolliver and co-workers, who observed the P(12) and P(13) lines in the fundamental vibrational band as well as the P(9)-P(11) transitions in the $v = 2 \leftarrow 1$ hot band with an accuracy of ~ 0.002 cm⁻¹.⁴ In 1982, Bernath and Amano reported the first observation of the low J transitions in the fundamental band, covering the P(4)-R(4) rovibrational transitions.⁵ After this work various studies of hot bands were published, including transitions from bound to quasibound states as well as quasibound to quasibound transitions.⁶⁻⁸ In 1989, Crofton and co-workers measured a few new transitions in the fundamental band along with several lines in the $v = 2 \leftarrow 1$ hot band as well as in the fundamental bands of the ³HeH⁺, ⁴HeD⁺, and ³HeD⁺ isotopologues.⁹ Pure rotational studies were first carried out by Liu *et al.* where the $J = 7 \leftarrow 6$ transition was measured,¹⁰ followed by the measurement of $J = 1 \leftarrow 0$ and $J = 2 \leftarrow 1$ by Matsushima *et al.*¹¹ as well as some low J

rotational transitions of the ³HeH⁺, ⁴HeD⁺, and ³HeD⁺ isotopologues. Higher J rotational transitions were measured by Liu and Davies^{8,12} with J as high as 25.

From a theoretical standpoint the HeH⁺ ion is a relatively simple species that is isoelectronic to H₂. This makes HeH⁺ an important benchmark molecule for high-level *ab initio* calculations that take into account not only non-adiabatic corrections to the Born Oppenheimer approximation, but also relativistic and quantum electrodynamic (QED) effects. Recent *ab initio* calculations by Pachucki and Kosama,¹³ which have treated the non-adiabatic corrections using Non-Adiabatic Perturbation Theory as well as the relativistic (α^2) and leading QED (α^3) corrections to the Born-Oppenheimer approximation, have been able to reproduce many experimentally measured rovibrational transitions with an accuracy on the order of 0.01 cm⁻¹ (~ 300 MHz). This sort of accuracy is only currently achievable for a select few molecular systems, namely, H₂, H₂⁺, H₃⁺, and HeH⁺.¹³⁻¹⁷ In order to predict transition frequencies with accuracies on the level of 0.001 cm⁻¹ or better for more complicated systems, it is imperative that the theoretical treatment of the aforementioned benchmark systems be well developed. Since theory must be informed by experiment to push the boundaries of these calculations, experimentalists need to provide highly accurate and precise measurements of molecular transitions for these species.

The HeH⁺ molecule has also proven to be a useful benchmark system for theoretical treatments that go beyond the Born-Oppenheimer approximation.¹⁸ These methods rely on using a set of correlated Gaussian functions that are functions of the separations between the nuclei and electrons, thus eliminating the traditional separation of the nuclear and electronic wavefunctions of the Born-Oppenheimer approximation. Within this framework the authors also developed algorithms for calculating the complete relativistic correction for this molecule.^{19,20} To date, these sorts of calculations have

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only been performed on states with no angular momentum (i.e., “rotationless” states).

Another approach has been to develop a global empirical potential that is based on the available spectroscopic data.²¹ This work used all available spectroscopic data from all isotopomers in a fit to a modified Lennard-Jones potential that is able to provide the correct behavior at large internuclear separations near the dissociation limit. This approach also allows for experimental determination of the Born-Oppenheimer breakdown functions which showed reasonable agreement with a fitted theoretical potential based on the calculations of Bishop and Cheung.²²

II. EXPERIMENTAL

The instrument used in this work has been described in detail in Ref. 23 and therefore will be described here only briefly. For this work, we used a technique that has been previously developed in our lab called Noise Immune Cavity Enhanced Optical Heterodyne Velocity Modulation Spectroscopy (NICE-OHVMS)^{23–25} which combines the high sensitivity of Noise Immune Cavity Enhanced Optical Heterodyne Molecular Spectroscopy (NICE-OHMS)²⁶ with the ion/neutral discrimination of velocity modulation spectroscopy.²⁷

The spectrometer is based on a commercially available continuous wave optical parametric oscillator (Aculight Argos 2400 SF) that is tunable across the 3.2–3.9 μm range. The pump laser (Koheras Adjustik Y-10) is phase modulated at a frequency of ~ 80 MHz to produce a pair of RF sidebands that are imprinted onto the idler wave. The idler wave is then coupled into an external optical cavity (finesse of ~ 150) which surrounds a liquid nitrogen cooled positive column discharge cell, in which ions of interest are produced from precursor gasses (a 2 Torr mixture of H_2 and He in a 1:100 ratio) and where their absorption profiles are velocity modulated. Light transmitted through the cavity is detected by a fast photodiode detector (Boston Electronics Vigo PVM-10.6-1 \times 1), from which the signal is demodulated at the same frequency used

to generate the 80 MHz sidebands, using a pair of frequency mixers that are 90° out of phase with one another. Further demodulation of the mixer outputs at twice the velocity modulation frequency (~ 80 kHz) is accomplished by a pair of lock-in amplifiers, which acts to recover the velocity modulation information.

Frequency calibration of our spectra was accomplished using an optical frequency comb (Menlo Systems FC-1500 with 100 MHz repetition rate) to measure the difference in frequency of the pump and signal beams at each point. Initial measurements of the frequencies of both beams (ten measurements for each) are performed using a near-infrared wavemeter (Burleigh WA-1500) to determine the mode number of the nearest comb tooth. The accuracy of the wavemeter was enhanced by measuring nearby reference lines of CH_4 .²⁸ These reference line frequencies are all determined to within ~ 5 MHz and any systematic errors introduced by the wavemeter can be corrected to ensure that the proper comb mode numbers are determined.

III. RESULTS

Figure 1 shows a typical NICE-OHVMS spectrum of the P(1) transition of HeH^+ at 85258146.86(35) MHz. The line-shapes have an odd symmetry resulting from the heterodyne detection and velocity modulation schemes. The narrow features near the center of the lines are blends of several individual Lamb dips that are spaced by half-integer multiples of the heterodyne frequency about the center of the transition. To extract the transition line centers, we fit the data from all four of the detection channels simultaneously (Figure 2) with some shared parameters between the data channels such as the line center, full-width of the blended feature, and the heterodyne detection angle. Further information regarding the fitting routines has been given by Hodges *et al.*²³

Table I shows that our measurements exhibit good agreement with the values measured by Bernath and Amano as all measured transitions lie within or only slightly outside their 30–60 MHz claimed uncertainties. However, in this work we

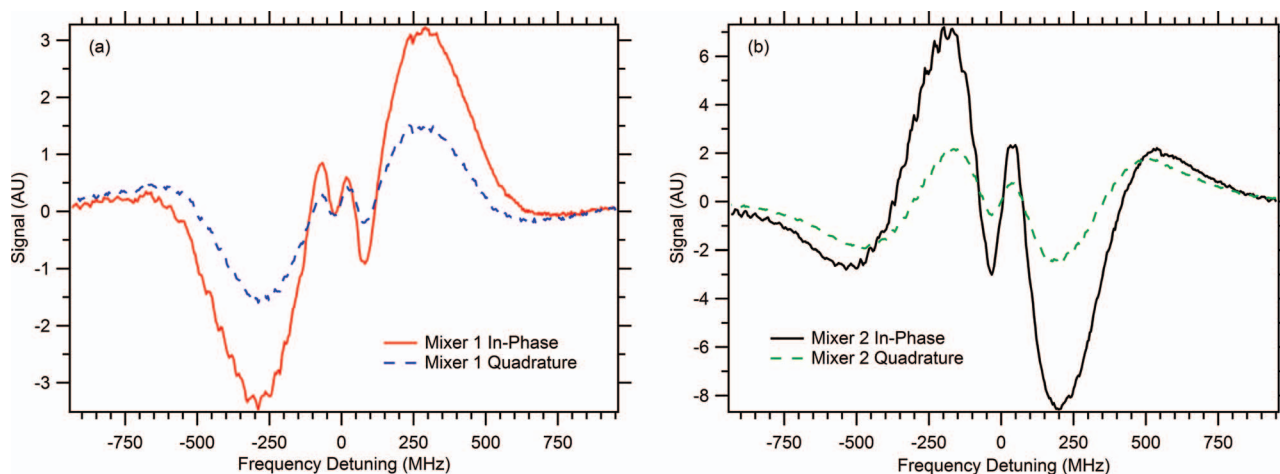


FIG. 1. Typical NICE-OHVMS scan of the P(1) fundamental band transition of HeH^+ showing the central Lamb dip feature sitting on top of the Doppler profile of the line. Signals from each of the four detection channels are shown with the in-phase (red solid trace) and quadrature (blue dashed trace) channels from mixer 1 plotted in panel (a) and the in-phase (black solid trace) and quadrature (green dashed trace) channels of mixer 2 in panel (b).

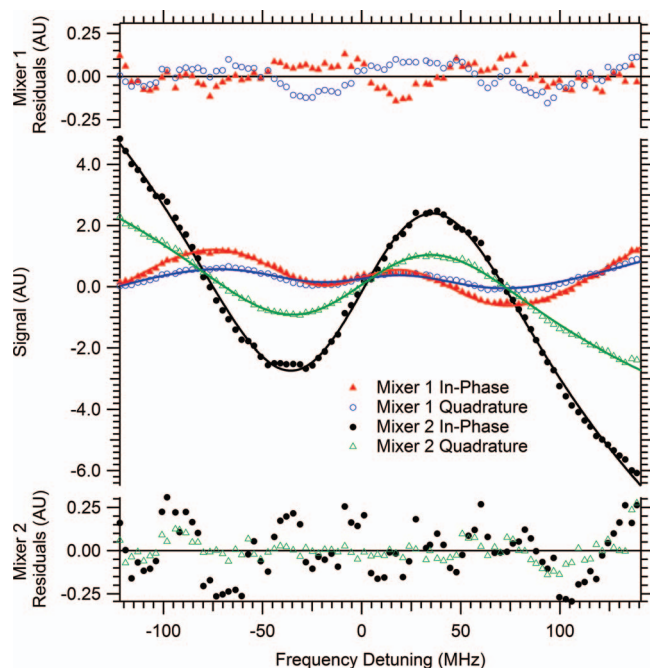


FIG. 2. Frequency comb calibrated scan of the central sub-Doppler Lamb dip feature in the P(1) rovibrational transition of HeH^+ , along with a simultaneous fit of all four data acquisition channels. Colored markers represent the experimental data, while the colored solid traces show the fit of the data to the equation outlined in Hodges *et al.*²³ Fit residuals from each detection channel are plotted on the upper (channels from mixer 1) and lower (channels from mixer 2) axes. For clarity, only every third data point is shown.

have improved the precision on these measurements by two orders of magnitude. For all of the measurements we were able to obtain precisions on the order of 1 MHz for the line centers due to both our ability to saturate the transitions which allows us to fit the relatively narrow sub-Doppler features, and the frequency calibration provided by the optical frequency comb which allows us to go far beyond the typical tens of MHz measurement uncertainty provided by mid-infrared wavemeters and Doppler-broadened reference gas lines.

These new measurements together with all available data for the fundamental band^{4,5,7,9} as well as pure rotational data^{8,10,11} were included in a fit to a power-series expansion of the vibration-rotation term values for a $^1\Sigma$ linear molecule as shown in Eq. (1) [The measurements of P(9)-P(11) by Purder *et al.* were not included in the fit as no uncertainties were

TABLE I. All measured rovibrational transitions in the fundamental vibrational band of HeH^+ and a comparison to those values measured by Bernath and Amano.⁵ All units are in MHz.

Transition	Freq.	St. Dev.	Prev. value ⁵	Diff.
P(3)	80795499.88	0.99	80795566.39	-66.51
P(2)	83096617.69	1.34	83096650.39	-32.69
P(1)	85258146.86	0.35	85258082.06	64.80
R(0)	89115533.66	1.38	89115502.62	31.04
R(1)	90788380.66	0.40	90788398.50	-17.84
R(2)	92275879.63	0.77	92275875.74	3.89
R(3)	93567523.38	0.92	93567519.55	3.82

TABLE II. Rovibrational parameters from a fit of experimentally measured rotation and rovibration transitions to Eq. (1). All units are in MHz.

Parameter	This work	Liu and Davies ⁸
ν_0	87268330.62(54)	87268319(33)
B_0	1006063.39(15)	1006063.3(45)
D_0	486.1762(187)	486.512(96)
H_0	0.1807358(2628)	0.18428(84)
$L_0 \times 10^4$	-1.17975(1418)	-1.331(36)
$M_0 \times 10^7$	0.73228(3114)	1.022(69)
$N_0 \times 10^{10}$	-0.49376(2392)	-0.702(48)
B_1	924550.54(17)	924554.8(45)
D_1	475.1636(138)	475.606(99)
H_1	0.1660888(3241)	0.17049(84)
$L_1 \times 10^4$	-1.31950(2056)	-1.499(33)
$M_1 \times 10^7$	1.05510(4957)	1.385(60)
$N_1 \times 10^{10}$	-1.12488(4121)	-1.352(42)

reported],²⁹

$$F_v = G_v + B_v J(J+1) - D_v [J(J+1)]^2 + H_v [J(J+1)]^3 + L_v [J(J+1)]^4 + M_v [J(J+1)]^5 + N_v [J(J+1)]^6. \quad (1)$$

The fit was performed using PGOPHER,³⁰ floating all parameters in both the ground and first excited vibrational states. In addition to our high-precision rovibrational measurements and the remaining fundamental band data, the fit includes the two pure rotational transitions ($J = 1 \leftarrow 0$ and $J = 2 \leftarrow 1$) measured by Matsushima *et al.* with very high precision (~ 200 kHz), as well as the pure rotational transitions of Liu and Davies, which includes 11 transitions in both the $v = 0$ and $v = 1$ vibrational states covering a range of J'' from 10 to 20. Parameters from the fit are given in Table II along with a comparison to those values obtained by Liu and Davies.⁸ Full details of the fit can be found in the supplementary material.³¹ Inclusion of these high precision measurements allows for a more precise determination (by roughly an order of magnitude) of the band origin as well as the B rotational constants and the lower order centrifugal distortion terms up to H.

It is interesting to note that for all the centrifugal distortion terms there are significant differences between our values and those of Liu and Davies. However, the results of the fit showed that the weighted residuals were randomly distributed across the entire range of J'' , which suggests that the differences in the fit parameters may be due to a high degree of correlation among the higher order parameters. Indeed, when the correlation matrix is examined it is clear that this is the case as the H, L, M, and N parameters all show correlations of ≥ 0.9 with each other.

Another comparison can be made to the fit produced by Matsushima *et al.*¹¹ In their fit they only included their $J = 1 \leftarrow 0$ and $J = 2 \leftarrow 1$ transitions along with the available rovibrational data in the fundamental band, while only including terms up to L (the values of L were fixed to the *ab initio* predictions of Bishop and Cheung²²). By doing so they were able to obtain very precise values for the B, D, and H values, which are nearly an order of magnitude more precise

TABLE III. Experimentally determined rotation-vibration energy levels $E(v,J)$ for ${}^4\text{HeH}^+$. All units are in MHz.

J	$E(0,J)$	$E(1,J)$
0	0	87268330.76(41)
1	2010183.86(20)	89115533.7(14)
2	6018916.87(28)	92798564.52(44)
3	12003064.7(11)	98294796.51(83)
4	19928164(60)	105570588.0(14)
5	29749118(30)	114581537(85)
6	41409933(172)	125273098(153)
7	54845432(194)	137580625(228)
8		151431127(245)

than the values reported in Table II. It may be the case, however, that the quality of their fit was somewhat fortuitous, due to the weighting of the highly precise values for the rotational transitions and their influence on the values of the lower order rotational parameters. We conjecture that since these lower order parameters were tightly constrained by only two transitions, their fit may have yielded well-determined parameters because there was so much more relative uncertainty in the rovibrational transition frequencies. The inclusion of our data, which also probe the $J = 0, 1,$ and 2 levels in the ground vibrational state and carry a similar weighting in the fit as Matsushima's rotational transitions, may explain the apparent increase in the uncertainty of our parameters.

To further assess the accuracy of our measurements we performed a test by adding Gaussian noise of varying amounts (as determined by the standard deviation of this added noise) to our transition frequencies and running the fit described above using these modified frequencies. For noise with a standard deviation of 2 MHz we begin to see a noticeable degradation in the quality of the fit in terms of the residuals of our seven measured transitions. With this amount of "noise" we find that the RMS of the residuals for these seven transitions increases by roughly a factor of two. Though this test may not be 100% conclusive due to the random nature of adding in this noise, it does give us confidence that our claimed uncertainties are appropriate in size.

Using these new data along with previous infrared and pure rotational work, a set of experimentally determined rovibrational energy levels can be derived using a combination difference analysis. Evaluating the energy levels in this way is advantageous because they are not based on any model Hamiltonian. The energy levels covering $J = 0-7$ in the vibrational ground state and $J = 0-8$ in the $v = 1$ vibrational excited state can be computed based on the available spectroscopic data. Table III summarizes the results.

The high precision (no larger than 1.4 MHz) of the $J = 3$ level in the ground vibrational state and the first five rotational levels in the $v = 1$ vibrational state, will allow these energy levels to serve as excellent benchmark values for new *ab initio* calculations on this molecule.

IV. CONCLUSION

We have performed sub-Doppler mid-infrared spectroscopy on the HeH^+ cation. By using the technique of

NICE-OHVMs in conjunction with frequency calibration provided by an optical frequency comb, we have re-measured seven fundamental band transitions of this molecule with a precision on the order of 1 MHz, and were able to achieve sub-MHz precision on most of the measured transitions. Using these new transitions with their improved uncertainties we have improved the values of the band origin as well as the B rotational constants and the lower order centrifugal distortion terms in a fit that includes all available spectroscopic data for the $v = 0$ and $v = 1$ states of the ${}^4\text{HeH}^+$ molecule. These new measurements also allowed for very precise determination of the low J rotation-vibration energy levels in the ground and $v = 1$ states, which will serve as new benchmarks for theorists to test *ab initio* calculations as higher level non-adiabatic, relativistic, and QED corrections are included. These measurements could also be used in a refinement of the empirical potential originally published by Coxon and Hajigeorgiou.²¹

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- ³¹See supplementary material at <http://dx.doi.org/10.1063/1.4895505> for the fit details of each experimentally measured transition.