Observation of the Infrared Spectrum of the Helium Molecular Ion $(^3\mathrm{He}\,^4\mathrm{He})^+$

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The vibration-rotation spectrum of the helium molecular ion $(^3\mathrm{He}\,^4\mathrm{He})^+$ has been observed for the first time. The Doppler-tuned ion-beam laser-resonance technique was used. Nine transitions in the fundamental band have been measured with an uncertainty of 0.0006 cm^{-1} or 0.3 ppm. The accuracy exceeds that of the available theory by more than 3 orders of magnitude.

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That the helium molecular ion plays an important role in helium afterglow plasmas is well known.[1] Recently the success of the nitrogen-ion laser pumped by charge transfer (CT) to $\mathrm{He_2}^+$ has focused attention on the CT interactions of $\mathrm{He_2}^+$ with other small molecules.[2] The ion is also of interest to quantum chemists because it is a comparatively simple multielectron system, consisting of only three electrons and two nuclei. In astrophysical situations, the ion may exist in the atmospheres of helium-rich stars and in ionized nebulae in sufficient quantities to affect the chemistry of those objects.[3]

The helium molecular ion was first identified by Tüxen[4] in 1936 in a mass spectrometer. Since then its mobility,[5] formation,[6,7] and recombination with electrons[8] have all been the subjects of many studies. Comparatively few spectroscopic data have been reported. Maas *et al.*[9] and Flamme, Mark, and Los[10] have measured translational spectra of $\mathrm{He_2}^+$, i.e., momentum distributions of the He^+ fragment from the rotational predissociation of $\mathrm{He_2}^+$ in a fast beam. Ginter and Ginter[11] have extrapolated $\mathrm{He_2}^+$ molecular spectroscopic constants from measured $p\pi$ Rydberg series of $\mathrm{He_2}$.

Maas *et al.* also calculated *ab initio* the electronic eigenenergy of the $\mathrm{He_2}^+$ ground state, and further adjusted their potential curve to fit the energies and widths of the quasibound levels they observed. There are many other theoretical works on the ion.[12] Most recently, Khan and Jordan[13] used the multiconfiguration self-consistent-field procedure to determine the potential curves of the first two electronic states of $\mathrm{He_2}^+$, and derived spectroscopic constants. As yet no theoretical treatment has included corrections beyond the simple Born-Oppenheimer approximation. Presumably this lack is due, at least in part, to the absence of pressure from precise experimental data.

We report in this Letter the first direct observation of the infrared (IR) vibration-rotation spectrum of the helium molecular ion. The $(^3\mathrm{He}\,^4\mathrm{He})^+$ isotopic form was studied because its mass asymmetry allows electric-dipole vibrotatory transitions. Nine R-branch transitions in the fundamental band of the electronic ground state have been detected. The experiment setup is similar to that previously used for HD^+[14] and several isotopic forms of HeH^+[15] and $\mathrm{D_3}^+$.[16] An ion beam of several kiloelectronvolts kinetic energy intersects nearly colinearly a CO IR laser beam of fixed frequency. The kinetic energy of the ions is tuned so that the Doppler shift brings an ion transition into resonance with the laser frequency.[17] After the interaction, the ion beam passes through a target-gas cell and the attenuated beam is collected in a Faraday cup. If the collision cross section depends on the internal state of the beam molecules, as is usual, the population redistribution caused by a resonant transition changes the amount of attenuation. This effect permits detection of the resonance by chopping of the laser beam and monitoring of the Faraday-cup current with a lock-in detector. For the work in this paper, helium was used as the target gas.

Because $\mathrm{He_2}$ has no natural bound state, $\mathrm{He_2}^+$ must be formed by chemical reactions. In our experiment, the ions are created in a coaxial hot-cathode controlled-electron-impact ion source.[18] There are two main channels[1] for $\mathrm{He_2}^+$ formation:

$$\mathrm{He}^* + \mathrm{He} \rightarrow \mathrm{He_2}^+ + e^-, \tag{1}$$

$$\mathrm{He}^+ + 2\mathrm{He} \rightarrow \mathrm{He_2}^+\mathrm{He}, \tag{2}$$

where He^* in the Hornbeck-Molnar[6] process (1) is a helium atom with $n \geq 3$. At high pressure, the three-body reaction[7] (2) dominates. The molecular ions formed in these reactions are in highly excited vibrational states. But subsequent collisions at our source pressures (> 1 Torr) deexcite the ions to their ground vibrational state,[19] probably completely. This is an advantage for the observation of the fundamental band absorption. However, complete deexcitation, if it occurs, will prevent us from observing hot bands with this ion source.

The source gas is a 1:1 mixture of $^4\mathrm{He}$ and $^3\mathrm{He}$. $^3\mathrm{He}$ is expensive. Therefore, to allow large flow rates and

TABLE I. Summary of the observed $(^3\mathrm{He}\,^4\mathrm{He})^+$ transitions. Also given are theoretical and He_2 Rydberg-series extrapolation results, with their differences from the experimental values in parentheses.

Experiment		Theory[b]		
Transition $(v',N')-(v'',N'')$	Frequency[a] (cm^{-1})	Khan and Jordan (cm^{-1})	Maas *et al.* (cm^{-1})	Rydberg-series extrapolation[c] (cm^{-1})
(1,2)-(0,1)	1781.8394	1780.18(−1.64)	1782.29(0.45)	1781.19(−0.65)
(1,4)-(0,3)	1810.7172	1808.99(−1.73)	1811.08(0.36)	1810.10(−0.62)
(1,5)-(0,4)	1824.2118	1822.46(−1.75)	1824.55(0.34)	1823.62(−0.59)
(1,6)-(0,5)	1837.0549	1835.28(−1.77)	1837.37(0.32)	1836.50(−0.56)
(1,7)-(0,6)	1849.2293	1847.43(−1.80)	1849.54(0.31)	1848.71(−0.52)
(1,8)-(0,7)	1860.7190	1858.91(−1.81)	1861.04(0.32)	1860.24(−0.48)
(1,10)-(0,9)	1881.5800	1879.74(−1.84)	1881.94(0.36)	1881.22(−0.34)
(1,11)-(0,10)	1890.9155	1889.07(−1.85)	1891.33(0.41)	1890.62(−0.30)
(1,12)-(0,11)	1899.5091	1897.65(−1.86)	1899.98(0.47)	1899.28(−0.23)

[a] Estimated 1-SD uncertainty is $0.0006\ \mathrm{cm}^{-1}$.

[b] Computed from interatomic potential points with cubic spline interpolation. Khan and Jordan is *ab initio* theory; Maas *et al.* is experimentally adjusted theory (see text).

[c] Calculated from spectroscopic constants scaled from Ref. 11.

long searching times, we built a helium recirculating system. Exhaust gas from the ion-beam line diffusion pumps is continuously scavenged and fed back into the ion source through a trap[20] filled with activated charcoal and zeolite and cooled with liquid nitrogen. Only helium ions, small amounts (<0.1%) of hydrogen-bearing ions, and traces of other impurities appear in the ion beam, as verified by a tunable Wien filter in the beam line, used as a mass spectrometer.

The attenuated ion current of $(^3\mathrm{He}\,^4\mathrm{He})^+$ is comparatively small, at 0.5–2.0 nA, depending on the acceleration voltage. The transition dipole moment of $(^3\mathrm{He}\,^4\mathrm{He})^+$ is also small because the mass asymmetry is slight. Therefore, compared with the previous experiments, longer integration time was needed. Additionally, the resonance predictions available left a large uncertain frequency range to search. Finally, the effectiveness of a target gas could not be assessed before the first resonance was found. Some obvious gas choices, such as H_2 and O_2, turned out to give no signal. Taken together, these factors made the search for the first resonance extremely time consuming. Once signals were seen, we used the frequency of each successive resonance to adjust the $(^3\mathrm{He}\,^4\mathrm{He})^+$ molecular constants progressively so as better to predict the next one. Fortunately, this process converged fairly quickly.

The CO laser is locked by use of a microcomputer[21] at either the center of its gain curve (single-mode lock) or the intersection of two adjacent single-mode gain curves (double-mode lock), with rms instabilities less than 4 or 0.3 MHz, respectively. In the search for resonances the single-mode lock was used to ensure maximum laser power. But in the determination of the resonance frequency, the more stable and precise double-mode lock was used whenever the laser power was sufficient. More than half of the resonances were observed with double-mode–locked laser lines.

Table I summarizes the experimental results. In addition to those seen, several other transitions were searched for. For the missing ones, either there were no matching $^{12}\mathrm{C}\,^{16}\mathrm{O}$ laser lines within the acceleration voltage limits of 2.5 to 9.5 kV, or the matching laser lines were inherently too weak, or they were absorbed by water vapor in the air. By changing to a different isotopic form of the laser gas, we should be able to find more fundamental-band ion resonances. Appropriate redesign of the ion source might let us see hot bands as well.

Kinematic compression in the accelerated beam[14] renders the resonance linewidths very narrow (of order 10^7 Hz). The residual width is due to the angular divergence of the two intersecting beams, the initial ion kinetic-energy spread, and any unresolved structure. Some high signal-to-noise-ratio lines, for example, $R(6)$, exhibit more than one peak (Fig. 1). These splittings apparently are caused by magnetic hyperfine interactions, chiefly of the electron moment with the $^3\mathrm{He}$ nuclear moment and the molecular rotation moment. Anomalies in the ion-beam velocity distribution due to source exit-hole collisions[15] may also be present. We plan a full hyperfine analysis. For this communication, in view of the often poor signal-to-noise ratio, we have simply reported in Table I the center of the strongest peak in each resonance pattern. These data may be shifted slightly [probably less than 1 SD (standard deviation)] from the pure vibration-rotation frequencies.

The 1-SD uncertainty ascribed to the frequency determinations includes an estimate of laser frequency instability and shifts with operating conditions, errors in the ion kinetic energy, and the error in laser-beam–ion-beam interaction angle. A quadratic sum yields $0.0006\ \mathrm{cm}^{-1}$, about 0.3 ppm of the transition frequency.

Table II shows the results of fitting the transition fre-

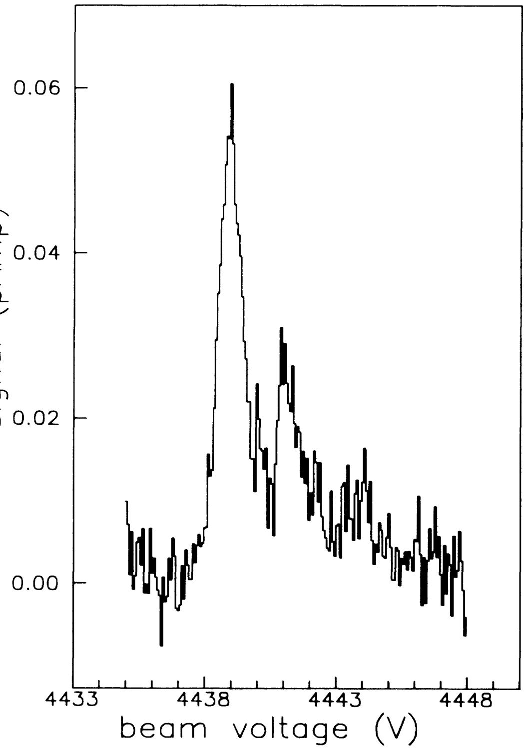

FIG. 1. A trace of the (1,7)–(0,6) transition of $(^3\mathrm{He}\,^4\mathrm{He})^+$ driven by a single-mode laser line, showing splittings believed due to hyperfine structure (see text). The voltage step is 0.07 V (0.5 MHz) with 16-sec integration time per step. The width of each peak is about 8 MHz and the splitting is about 14 MHz.

TABLE II. The fitted Dunham coefficients.

Coefficient	Fitted values (cm $^{-1}$)
$Y_{10}(\omega_e)$	1832.735 57(0.019)[a]
$Y_{20}(-\omega_e X_e)$	−41.1[b]
$Y_{01}(B_e)$	8.413 427 55(0.017)
$Y_{11}(-\alpha_e)$	−0.292 107 61(0.0069)
$Y_{02}(-D_e)$	$2.211\,15\times10^{-4}(3.6\times10^{-4})$
$Y_{12}(-\beta_e)$	$1.180\,83\times10^{-4}(8.3\times10^{-5})$
$Y_{03}(H_e)$	$6.249\,31\times10^{-7}(3.9\times10^{-7})$

[a] The numbers in parentheses are the fitting errors of the coefficients.
[b] Y_{20} was held constant during the fitting at the value of Ref. 11.

quencies by a Dunham series containing one fixed and six adjustable coefficients. The standard deviation of the fit is 0.0006 cm $^{-1}$. These spectroscopic constants cannot be considered unique, because the lack of P-branch $v=1$ to $v=0$ band data, and of data for other bands, leaves strong correlations among them. Nevertheless, the coefficients should be useful in prediction of the missing lines in the 1- to 0-band R branch.

To predict transition frequencies for the initial search, we scaled the Rydberg-based spectroscopic constants of $^4\mathrm{He}_2{}^+$ from Ref. 11 to the reduced mass of $(^4\mathrm{He}\,^3\mathrm{He})^+$ according to the relationship[22]

$$Y^i_{jk} = (\mu/\mu^i)^{j/2+k} Y_{jk}, \tag{3}$$

where Y_{jk} are Dunham coefficients, μ is the reduced mass, and i indicates the isotopic form. The resulting transition predictions, listed in Table I, show reasonable agreement with the measured values.

Also listed in the Table I are two sets of theoretical transition frequencies which we calculated from the potential curves of Khan and Jordan[13] and Maas *et al.*[9] using the Cooley-Numerov method.[23] Khan and Jordan used 113 configurations to obtain the potential curve in the Born-Oppenheimer approximation. The largest corrections to this approximation take into account the coupling of electronic and nuclear motions. For HeH$^+$ this correction is about 2 cm $^{-1}$.[15,24] The correction for He$_2{}^+$ should be of comparable size or moderately smaller. Thus the theories, within their limitations, are consistent with experiment. The experimentally adjusted potential of Maas *et al.* gives more nearly correct transitions than does the *ab initio* potential of Khan and Jordan. The energy levels of Maas *et al.*'s unadjusted *ab initio* potential, which we computed but do not show, are farther off still. The errors of these results are unknown. But judging by the changes we could induce by varying the method used to interpolate between potential points in the Cooley-Numerov calculation, we believe that the uncertainties in the theoretical frequency predictions exceed 1 cm $^{-1}$.

We have presented in this Letter the first observation of the $(^3\mathrm{He}\,^4\mathrm{He})^+$ vibration-rotation spectrum. The accuracy of our measurements greatly exceeds that of available theoretical calculations. A detailed analysis of the hyperfine and spin-rotation structure remains to be done. We hope that our work will stimulate improved quantum chemical calculations on this simple molecule. An extensive high-accuracy $(^3\mathrm{He}\,^4\mathrm{He})^+$ spectrum might provide a useful new diagnostic for isotopic helium plasmas and, perhaps, an avenue to the interstellar detection of ^{3}He.

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