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Emission Spectra of Bound Helium Hydride

W. Ketterle, H. Figger, and H. Walther
Max-Planck-Institut für Quantenoptik and Sektion Physik, Universität München, D-8046 Garching bei München, Federal Republic of Germany

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The first observation of transitions between bound electronic states of neutral helium hydride is reported. Excited molecules were produced by electron transfer to the corresponding molecular ions. Emission spectra in the visible were obtained. Five electronic bands could be identified for three isotopic mixtures. Molecular constants confirming recent calculations of potential curves were derived for the first time. Predissociation of the upper state occurs for ^{4}HeH in contrast to ^{3}HeD. Also NeH spectra could be obtained by the same method.

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Helium hydride is one of the most elementary molecules. The ground state is repulsive, as shown by numerous experiments and calculations (see, for example, the references given in Theodorakopoulos *et al.*[1]) More than twenty years ago Michels and Harris[2] predicted that bound, excited states of helium hydride should exist. Their results were confirmed by the more accurate calculations of Slocomb, Miller, and Schaefer[3] and recently by the extensive study of Theodorakopoulos *et al.*[1] of six bound, excited states all showing Rydberg character. Autoionizing states have also been studied, both experimentally and theoretically.[4,5] However, there is only one experiment supporting the existence of bound, excited states of HeH. Möller *et al.*[6] irradiated a mixture of He and H_2 with synchrotron radiation and observed broad-band uv emission, which was assigned to a bound-free transition in HeH with the aid of theoretical potential curves. On the other hand, for ArH Johns[7] observed discrete optical spectra in a gas discharge, and it was not clear why the search for equivalent emission of HeH failed.[7] In this Letter we report the first observation of such discrete emission spectra, which are the ultimate proof that bound states of helium hydride exist.

We produced HeH by electron transfer to HeH^+ ions. The setup was similar to the one used to study neutral triatomic hydrogen.[8,9] However, the apparatus had to be considerably improved, since the HeH emission intensity was an order of magnitude smaller than that of D_3. The HeH^+ ions were produced in a discharge in a 10:1 mixture of helium and hydrogen. The ion beam was accelerated to 15 kV, mass analyzed by a magnetic sector field, and neutralized in a charge-exchange cell filled with alkali vapor. The light emission of excited HeH was analyzed by a 60-cm monochromator and the light intensity recorded by a photomultiplier and a photon-counting system. For the observation of the light emitted by the fast HeH molecular beam a special design of the optical imaging system was required[10] in order to obtain high detection efficiency and to reduce the Doppler broadening due to the spread angle of the detection system to below 1 Å. The instrumental width of the monochromator was adjusted to be between 1 (Fig. 1) and 4 Å (Fig. 2) depending on the intensities of the investigated spectra.

So far we have examined ^{3}HeH, ^{4}HeH, and ^{3}HeD and observed electronic bands near 8000, 6000, 5300, 4600, and 4100 Å. Corresponding lines of the different isotopic mixtures show an isotope shift of several angstroms. The spectra remained unchanged when potassium instead of cesium was used as the charge-transfer medium. As the masses of the neutralized ions were determined by the mass spectrometer, it was definitely proved that all the observed bands were due to the diatomic helium hydride molecule. (It can be ruled out that HeH^+ is responsible for the spectra because the excited states of this ion were predicted[11] to be unstable or only weakly bonding, with bond lengths several times as large as those derived from our measurements.)

We started our work with ^{4}HeH and obtained spectra which did not have the typical appearance of spectra of diatomic molecules. We then produced ^{3}HeD and around 8000 Å obtained the spectrum shown in Fig. 1. This spectrum is identified as belonging to a $\Sigma \rightarrow \Sigma$ transition. The peaks $R(0)$ to $R(20)$ and $P(1)$ to $P(13)$ could be assigned, and we could fit the whole spectrum, using the molecular constants given in Table I, with a maximum deviation of about 1.5 cm^{-1}, i.e., half a linewidth. The best fit of the observed intensity distribution was achieved with an effective rotational temperature of 3100 K. As the spectra have not been corrected for the spectral sensitivity of our detection system, the observed intensity of lines at longer wavelengths is smaller than in the simulation.

We then modified the molecular constants (B and D) according to the isotope relations and simulated the corresponding band of a ^{4}HeH spectrum. Almost all peaks observed could then be assigned, and the constants had to be varied by just a few percent to yield an

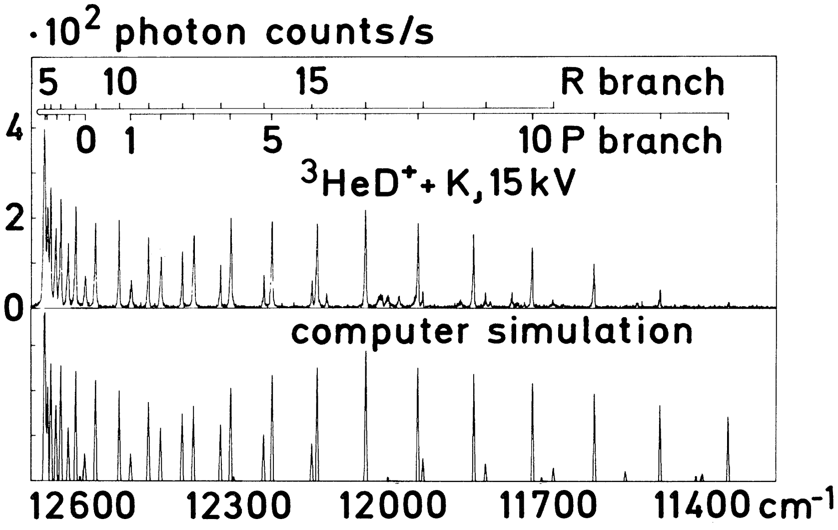

FIG. 1. Emission spectrum of ^{3}HeD near 8000 Å as obtained when the neutralized beam is observed 5 mm behind the alkali cell. The assignments are given at the top of the figure. The computer simulation was performed with the constants of Table I.

almost perfect fit to all lines identified [Fig. 2(a)]. The maximum deviation was a quarter of a linewidth, which was about 7 cm^{-1} for this spectrum. The rotational temperature (3000 K) was chosen similar to that in the case of ^{3}HeD. However, the intensity distribution strongly deviates from the experiment. $R(9)$, $R(10)$, $R(11)$, and $R(14)$ are much stronger than expected. We then compared two spectra emitted by the beam 5 and 15 mm behind the charge exchange cell [Fig. 2(b)], corresponding to a difference in time

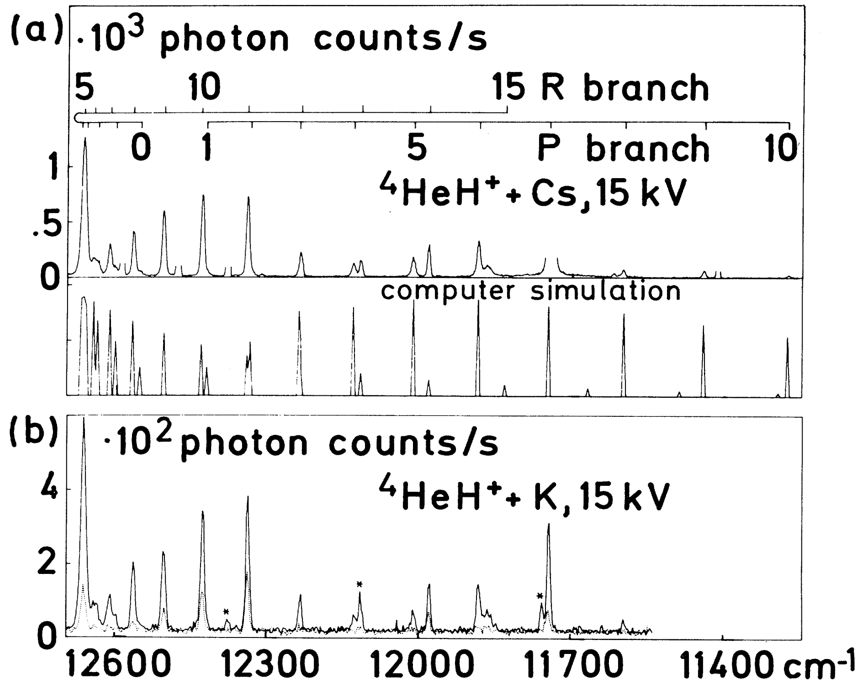

FIG. 2. (a) Emission spectrum of ^{4}HeH near 8000 Å observed 5 mm behind the charge-exchange cell. Lines of excited Cs have been omitted from the drawing. (b) Emission spectrum of ^{4}HeH observed 5 (solid line) and 15 mm (dotted line) behind the charge-exchange cell, demonstrating the different lifetimes of different rotational levels. Lines marked by an asterisk are at least partly due to emission of excited potassium.

TABLE I. Molecular constants for two isotopic mixtures of helium hydride determined by a least-squares fit. The primed and double primed quantities refer to the upper and lower states. v_0 is the band origin, B the rotational constant, and D the constant for centrifugal distortion. The bond lengths r were calculated from $B = h/8\pi^2 c\mu r^2$ with the reduced mass μ, and the vibrational frequencies ω were roughly estimated from the relation $\omega^2 = 4B^3/D$. The numbers in parentheses give the accuracy in units of the last digit corresponding to three standard deviations of the least-squares fit. The error for v_0 contains the uncertainty of the wavelength calibration.

Constant	^{4}HeH	^{3}HeD	Unit
v_0	12 489(5)	12 548(3)	cm^{-1}
B'	30.4(2)	20.51(6)	cm^{-1}
D'	0.0134(7)	0.0061(2)	cm^{-1}
B''	36.5(2)	24.60(6)	cm^{-1}
D''	0.0142(11)	0.0065(3)	cm^{-1}
r'	1.57	1.56	bohr
r''	1.43	1.42	bohr
ω'	2896	2376	cm^{-1}
ω''	3701	3022	cm^{-1}

of flight after generation of 13 ns. Only the anomalously strong peaks survived, indicating a lifetime of 10 to 15 ns for the upper levels of these lines, the lifetimes of the other levels being much shorter. As the radiative lifetimes are approximately the same for different rotational levels, we conclude that nonradiative transitions from the upper state crucially depend on the rotational quantum number and distort the intensity distribution of the emission spectra. As predissociation in hydrides is often caused by tunneling,[12] the difference of the reduced masses of ^{3}HeD and ^{4}HeH can account for the different behaviors of the two isotopic molecules. Accurate lifetime measurements, as we have already made for triatomic hydrogen,[8,9] are in progress and will give more information about this process and the potential curves involved.

Taking the vibrational frequencies from Table I and calculating how much the vibrational zero-point energy differs between the upper and the lower states, we obtain 403 cm^{-1} for ^{4}HeH and 323 cm^{-1} for ^{3}HeD. The difference between these two values is close to that between the band origins in Table I. No vibration is therefore excited in either the upper or the lower state. For further assignments we use the calculations of the potential curves of Theodorakopoulos *et al.*[1] For a $\Sigma \rightarrow \Sigma$ transition near 8000 Å there are two candidates: $F \rightarrow C$ and $C \rightarrow A$, this being the notation used in Ref. 1. The second possibility seems more likely for two reasons: First, the charge-transfer process will populate the lower-lying C state more strongly than the F state because of a smaller energy defect. Second, the calculated potential minima (from Fig. 1 of Ref. 1) are about 1.55 bohrs for the F and C states and about 1.45 bohrs for the A state. With the assignment $C \rightarrow A$, this would perfectly agree with our measured bond lengths in Table I. It should be pointed out that our measured B values are close to the one obtained for the HeH$^+$ ion theoretically[13] and experimentally.[14] This is a further indication that the observed levels of HeH are Rydberg states.

The other electronic bands observed for HeH are probably also 0-0 bands because the isotope shift of prominent lines is approximately 100 cm^{-1} or less. They seem to belong to transitions between Rydberg states with the main quantum number $n \geqslant 3$ and $n = 2$. The calculations of Theodorakopoulos *et al.* suggest the assignments $F \rightarrow A$, $F \rightarrow B$, D and $E \rightarrow A$, and D and $E \rightarrow B$ for the observed bands near 4100, 4600, 5300, and 6000 Å, respectively. Their rotational structure could not yet be assigned.

Because of the abundance of He and H$_2$ in stellar atmospheres and interstellar space, HeH is expected to be formed there. Therefore our data may be useful to find the HeH lines there.

By the same method, we recently observed emission spectra of ^{20}NeH and ^{22}NeH, which are strongest near 6850 and 7600 Å. These results, as well as an analysis of the other helium hydride bands, will be published elsewhere.

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