Observation of Fluorescence of the HeH Molecule

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This Letter reports the first spectroscopic detection of HeH, the simplest excimer molecule that can exist. HeH* is produced in electronically excited states in reactions between He and H_2 excited selectively by synchrotron radiation into the $C\,^1\Pi_u$ $(v' \geqslant 1)$ or $B\,^1\Sigma_u^+$ $(v' \geqslant 11)$ state. HeH* emits a broad characteristic fluorescence continuum between 200 and 400 nm which is attributed to $B\,^2\Pi \rightarrow X\,^2\Sigma^+$.

PACS numbers: 33.20.Lg, 33.50.—j, 34.50.—s

HeH is one of the smallest molecular systems and has attracted theoretical interest for a long time.[1,2] Its ground state is strongly repulsive; however, strongly bound excited states were predicted by a molecular-orbital calculation twenty years ago.[2] The main contribution to the bond is the polarization of the He atom by the H^+ core if H penetrates the electronic cloud of He. For the lowest excited states, $A\,^2\Sigma^+$ and $B\,^2\Pi$, a binding energy of ~ 2 eV was predicted.[2] Recently, more sophisticated *ab initio* calculations have underlined the existence of bound excited states.[1]

To the best of our knowledge, up to now no spectroscopic evidence of bound excited states of HeH has been found. The same is true for the other rare-gas hydrides with the only exception being ArH. Johns[3] reported infrared fluorescence bands in a gas discharge which he ascribed to a $^2\Pi \rightarrow {}^2\Sigma^+$ transition of ArH. Very recently, Sadeghi *et al.*[4] assigned a fluorescence continuum in the uv region which is generated in reactive collisions of thermal Ar metastables with H_2 to ArH emission.

In this paper we report on the first spectroscopic proof of the existence of rather long-lived excited states of HeH. They lead to broad uv bound-free fluorescence continua terminating at $X\,^2\Sigma^+$. Similar results were also obtained for the other rare-gas hydrides.[5] Here we concentrate on HeH, which is most important from the theoretical point of view.

Electronically excited HeH molecules were obtained from elementary reactions of the type

$$He + H_2^* \rightarrow HeH^* + H \tag{1}$$

in H_2-doped He. The pressures ranged between 0 and 10 Torr H_2 and 1 and 20 Torr He. Primary excitation of H_2 was performed optically with synchrotron radiation on the SUPERLUMI beam line at HASYLAB.[6,7]
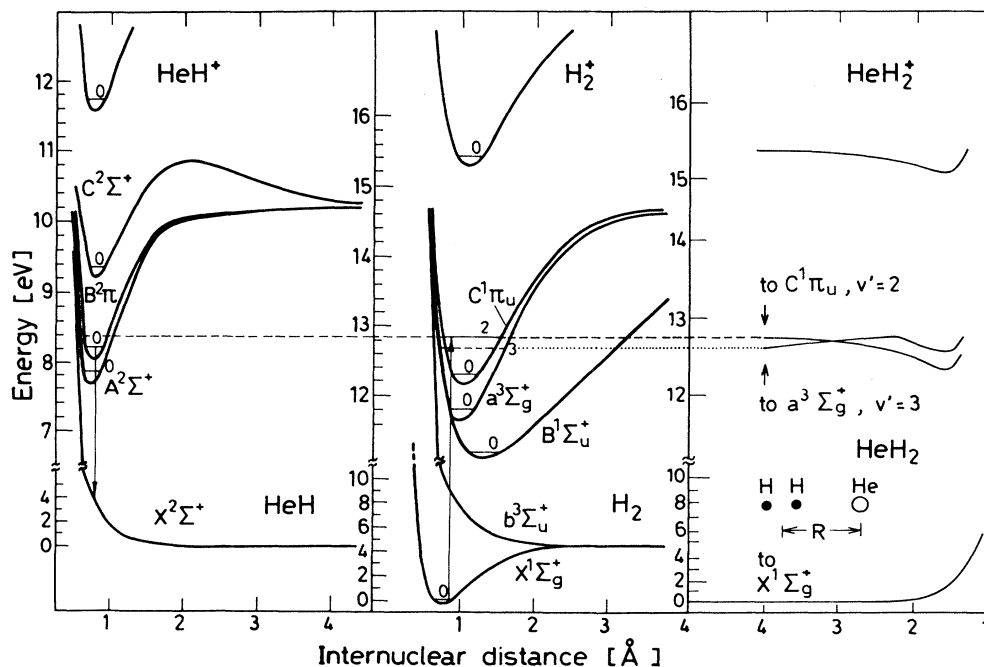

FIG. 1. Potential curves of selected states of H_2, HeH, and HeH$_2$. Data are taken from Refs. 1,8 and 9.
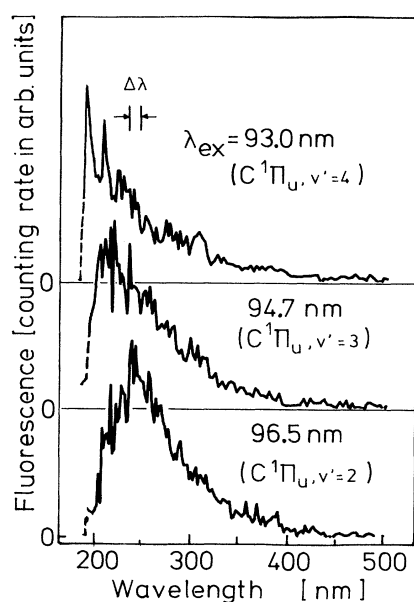
FIG. 2. Fluorescence of HeH ($B\,^2\Pi \rightarrow X\,^2\Sigma^+$) for different excitations into H_2 $C\,^1\Pi_u$. The spectra are corrected for the spectral response of the system; below 200 nm they are uncertain because of the cutoff of the response function.

The spectral resolution was sufficiently high for rotationally selective excitation of H_2.

Figure 1 shows the calculated potential curves of HeH[1] and those H_2 potential curves[8] which are important for this paper. If we assume optical excitation, it immediately follows from Fig. 1 that H_2 has to be excited either into high vibrational levels of the B state

or into the C state. Therefore, excitation wavelengths below the LiF cutoff are required. For this reason, the gas cell used was equipped with a thin In window (thickness 100 nm).

The fluorescence light was analyzed perpendicular to the exciting beam with a band pass of 10 nm. The signal-to-noise ratio was improved substantially by exploitation of the time structure of synchrotron radiation. Fluorescence was recorded only within a short time window (~ 10 ns) immediately following the excitation pulses (FWHM ~ 150 ps, repetition rate 1 MHz). The length of the time window roughly corresponds to the lifetime of the emitting state.

Fluorescence spectra which are observed following selective excitation of $v'=2$, 3, and 4 of the $C\,^1\Pi_u$ state of H_2 in a mixture of 0.3 Torr H_2 and 20 Torr He are shown in Fig. 2. For the lowest excitation energy, a broad, asymmetric continuum is observed with a maximum at 235 nm. With increasing excitation energy, the continuum further broadens and shifts to shorter wavelengths. For $v'=4$ excitation it already reaches the cutoff of the transmission of the monochromator (dashed part of the curves).

The observed spectra are ascribed to the decay of HeH created via (1). Between the two HeH excited states ($A\,^2\Sigma^+$ and $B\,^2\Pi$) which have to be taken into consideration as emitting states (see Fig. 1), we prefer to assign the emission to $B\,^2\Pi \rightarrow X\,^2\Sigma^+$ transitions. Johns[3] showed that the $A\,^2\Sigma^+$ state of ArH strongly predissociates. Because of the great similarities among the rare-gas hydride electronic structure, the same may hold also for HeH.
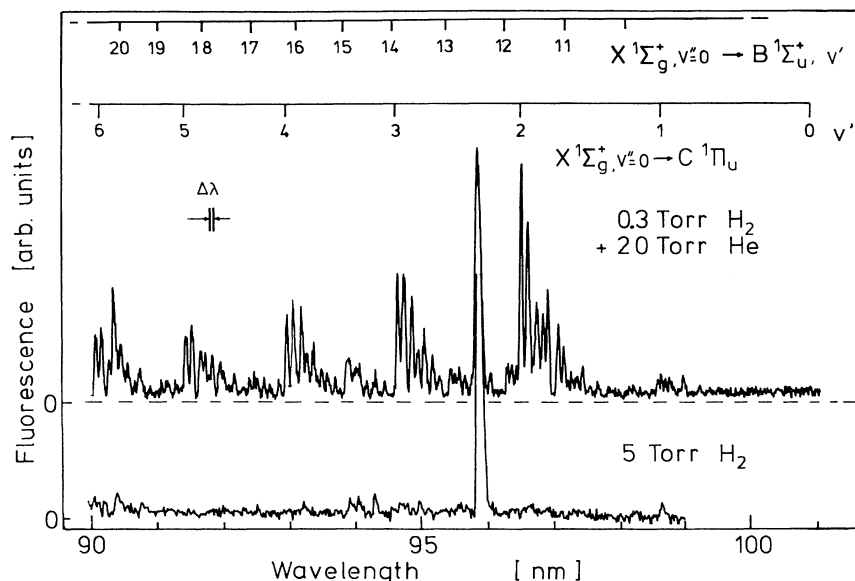
It must be pointed out clearly that in the wavelength

FIG. 3. Excitation spectrum of near-uv fluorescence (210–350 nm) of pure H_2 (5 Torr) and a mixture of 0.3 Torr H_2 and 20 Torr He.

range of the observed emission, in, e.g., gas discharges, the $a\,^3\Sigma_g^+ \to b\,^3\Sigma_u^+$ continuum of H_2 is also emitted.[10] Though optical excitation of H_2 in the H_2-He mixtures terminates at *ungerade* singlet states, one has to take into consideration collision-induced intersystem crossing (ISC), leading to population of the H_2 $a\,^3\Sigma_g^+$ state and its subsequent emission. The results presented now strongly support our assignment of the observed fluorescence.

In Fig. 3 we present excitation spectra of the fluorescence emitted in the wavelength interval 210–350 nm. The lower curve was obtained from 5 Torr H_2 without He. All the observed lines can be ascribed to N_2 impurities. Though the contamination of H_2 by N_2 was small (< 200 ppm), the N_2 excitation lines (e.g., at 95.8 nm) show up because they lead to the allowed $C'\,^1\Sigma_u^+ \to a\,^1\Sigma_g^+$ and $b\,^1\Pi_u \to a\,^1\Sigma_g^+$ transitions which emit within the wavelength interval of observation.[11] Following primary excitation of H_2 itself, no emission between 210 and 350 nm was observed. This shows that, even at the relatively high gas pressure used, in pure H_2 the collision-induced ISC can be neglected.

In the presence of He (upper curve; 20 Torr He + 0.3 Torr H_2) clearly the rotational lines of the $C\,^1\Pi_u$ state ($v'=2,3,4,5$; $v'=1$ very weak) are resolved. No signal is observed under $v'=0$ excitation. In addition to the C state, rotational lines of the B state ($v'\geqslant 11$) are observed, with smaller intensity, however. Various band heads of transitions to the B and the C states are marked in Fig. 3.[8]

The excitation spectrum clearly yields a threshold for the population of the emitting state. In the crudest approximation one might take the energy of $v'=1$ of the H_2 C state as the threshold energy. It correlates well with the theoretical prediction for the energetic threshold of the elementary reaction (1) which can be deduced from the calculated potential curves.[1] This is a strong support for our assignment of the observed emission. The other rare-gas–H_2 systems also all have a clear onset of the rare-gas hydride emission.[5] The individual onsets, however, are markedly different in agreement with the different binding energies of the emitting states involved. For the H_2-Ar system, we wish to point out that the threshold of the emission ascribed to the ArH molecule is significantly below the minimum of the H_2 $a\,^3\Sigma_g^+$,[5] in agreement with the data of Sadeghi *et al.*[4] From the observed onsets and the well-known dissociation limits of the rare-gas hydride $B\,^2\Pi$ states (He $^1S + H^*\,^2P$), the binding energies of the B states can be estimated. Results are given in Table I and compared with theoretical predictions. Two values for the well depth are available for HeH. The experimental value for the dissociation energy of the B state is in good agreement.

Now we may comment on the spectral distribution of HeH emission for different excitation energies (Fig.

TABLE I. Dissociation energies (D_0) of rare-gas hydride $B\,^2\Pi$ states [terminating at $H^*(^2P)$] in comparison with calculated binding energies (D_e).

|	D_0 (eV) This work	D_e (eV) Theory
HeH	2.05	2.20[a]
		1.94[b]
NeH	1.80	1.67[a]
ArH	2.93	2.75[a]
KrH	2.9	
XeH	$\geqslant 3.6$	

[a]From Ref. 1.
[b]From Ref. 2.

2). Following H_2 C ($v'=2$) excitation near to the threshold, in the subsequent elementary reaction (1) predominantly HeH B ($v'=0$) molecules are produced. The decay of such vibrationally relaxed molecules into a strongly repulsive final state leads to a broad, single-centered band in agreement with observation. With increasing excitation energy, higher vibrational levels of the HeH B state may be populated. This explains the observed broadening. The shift to shorter wavelengths is ascribed to an effect of Franck-Condon factors and the v^3 dependence of the transition probabilities. We should also mention that fluorescence from the energetically nearest level $v'=3$ of the H_2 $a\,^3\Sigma_g^+$ state looks completely different.[10]

We also measured fluorescence spectra of 10 Torr He doped with 0.3 Torr H_2 including the vacuum-uv spectral range. Bound-bound H_2 $C \to X$ transitions around 120 nm and bound-free fluorescence of the H_2 B state around 160 nm, emitted at large internuclear distances,[12] and the broad continuum of HeH at 235 nm were observed.

The intensity ratio of H_2 and HeH fluorescence gives a rough estimate of the total cross section, σ_f, of the reaction

$$H_2\,C\,^1\Pi_u\,(v'=2) + He \to HeH\,B\,^2\Pi + H. \qquad (2)$$
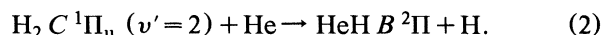
The Franck-Condon factors of H_2 $C \to X$ and $B \to X$ transitions are known well enough[13] to calculate the total H_2 fluorescence intensity from the observed part of the spectrum. With neglect of additional quenching of H_2 and HeH fluorescence (which is justified in view of the low gas pressures used), the ratio of the fluorescence intensities is then given by

$$I_{HeH}/I_{H_2} = \Gamma_f/\Gamma_{rad}. \qquad (3)$$

Γ_f is the rate of formation of HeH, and Γ_{rad} is the radiative decay rate of the primarily excited H_2 molecule which was measured separately. Γ_f obtained from (3) is finally converted into σ_f with use of classical kinetic expressions. As a result, we obtain $\sigma_f = 1.6 \pm 1$ Å^2 for

the C ($v' = 2$) state. This is an average value concerning the rotational quantum number ($J' \leq 3$). Although the estimate of σ_f is only approximate, the order of magnitude is important to rule out that the observed fluorescence around 235 nm is due to emission of the H_2 $a\,^3\Sigma_g^+$ state.

For C ($v' = 1$), the cross section seems to be much smaller. This may be explained in the following way. A more rigorous evaluation of the threshold for the elementary reaction (2) has to take into account also endothermic reactions of particles in the tail of the Maxwellian velocity distribution, and would place the energetic threshold somewhere between $v' = 1$ and 2. However, it is not the purpose of this paper to discuss these details.

Now we estimate the cross section for the reaction

$$H_2\, C\,^1\Pi_u\ (v' = 2) + He \rightarrow H_2\, a\,^3\Sigma_g^+ + He. \qquad (4)$$
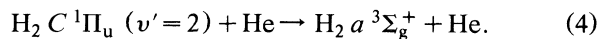
From the H_2 potential curves (Fig. 1) it follows that collision-induced ISC of C ($v' = 2$) and a ($^3\Sigma_g^+$) most probably populates $v' = 3$ of the a state because of the small energetic distance. This is also reasonable in view of calculated potential surfaces of the HD + He system.[9] In their paper Römelt, Peyerimhoff, and Buenker present results for He + HD ($C\,^1\Pi_u$) and of He + HD ($a\,^3\Sigma_g^+$), both for $v' = 0$ and different geometries.[9] By adding the known vibrational energies, we obtain the corresponding curves for $v' = 2$ (C state) and $v' = 3$ (a state) shown in the right part of Fig. 1 (collinear geometry). They may be a good estimate for the He + H_2 system. The curves cross one another at a distance of about 3 Å between the He atom and the center of H_2.

During the collision, the g/u symmetry of the dissociation limits is destroyed. The spin-orbit and spin-spin interactions lead to a perturbation in the crossing region, and the resulting adiabatic potential curves yield an energy gap. As an upper limit, we tentatively took twice the spin-orbit interaction energy $E_{s.o.} = 0.3$ cm^{-1}, of the atoms.[14]

The probability for the $C \rightarrow a$ transition during one passage of the crossing region is estimated with the Landau-Zener probability[15]

$$p = 1 - \exp\{-4\pi^2 \Delta E^2 / hv |\Delta F|\}. \qquad (5)$$

$2\Delta E$ is the width of the gap, F is the difference of the gradients of the diabatic potential curves, and v is the relative velocity of the particles in the crossing region. With $2\Delta E = 0.6$ cm^{-1}, $|\Delta F| = 3 \times 10^{-10} N$, and $v = 2.2 \times 10^3$ ms^{-1}, we obtain $p = 3.3 \times 10^{-6}$.

This value must be compared with the yet unknown probability, p_R, of reaction (2). As an estimate, we take the calculated probability of the reaction $H_2^+ + He \rightarrow HeH^+ + H$, which is about 10^{-1} to 5×10^{-1}.[16] The result of Stroud et al.[16] is valid for the direct reaction without a long-living intermediate collision complex. The potential surfaces of H_2 (C) + He and H_2^+ + He are very similar (see Fig. 1). Therefore, in the reaction of the neutrals, a long-living collision complex is not expected, either. It is obvious that the ISC probability cannot compete with the probability of the chemical reaction. It is interesting to note that the cross section for $H_2^+ + He \rightarrow HeH^+ + H$, $\sigma \approx 1$ Å^2,[17] is similar to our result, $\sigma_f = 1.6$ Å^2, ascribed to H_2 (C) + He $\rightarrow$ HeH + H.

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