Emission Spectra of Helium Hydride at 4.2 K

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Emission in the visible has been observed from dense, cold helium gas in contact with solid hydrogen when irradiated by a 15-MeV proton beam. All four stable isotopic combinations have been studied, and the spectrum of one of them, ^{4}HeD, appears highly perturbed. Spectral identification of rotational features and a plausible explanation of the perturbation have been provided by rovibrational energy-level calculations.

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Interest has been aroused by the recent observations of radiative transitions from the molecule HeH.[1,2] Though the electronic ground state of HeH is strongly repulsive, bound, excited Rydberg states can be expected like those of He_2, which also has a repulsive ground state. However, He_2 emission was first observed in 1913,[3] while HeH stability was only predicted in 1963[4] and confirmed in 1969,[5] and emission spectra were finally observed in 1985.[1,2] Whereas He_2 emission can be observed by striking of a discharge in relatively dense (~100 Torr) helium gas, such is not the case for HeH emission from mixtures of helium and hydrogen.[6] Of the successful experiments prior to our own, only one was able to obtain a discrete Rydberg spectrum and that was not from a gas mixture but by neutralization of an HeH^+ beam. More recently, additional experiments utilizing HeH^+-beam neutralization have been performed.[7-9]

Our experiment is capable of producing a discrete emission spectrum of HeH from an *in situ* combination of helium and hydrogen. The spectrum so obtained has been analyzed with the help of rovibrational energy-level calculations using the computer code of LeRoy[10] and the *ab initio* potentials of Theodorakopoulos *et al.*[11] This analysis has helped to identify the spectra and to give a plausible explanation for an anomalous spectrum obtained for ^{4}HeD.

This laboratory is engaged in the study of the spectroscopy of the solid hydrogens undergoing proton-beam irradiation.[12] We commenced a series of experiments starting with helium-doped samples of solid hydrogen whose explication will be presented elsewhere. One result, relevant to this work, is that the spectrum of such helium-doped samples is similar to that of dense, cold helium gas when irradiated by a 15-MeV proton beam. Such pure He-gas spectra, composed almost entirely of He_2 bands, at 4.2 K, have intensities very different from room-temperature discharges and, in fact, disappear as the sample is warmed to 20 K. Cold-helium-gas spectra, similar to ours but obtained by nitrogen-ion bombardment, have recently been reported by Kimura.[13]

It is an easy matter to control the pressure of helium/hydrogen mixtures at cryogenic temperatures. One need only admit some hydrogen to the sample cell, freeze it, and then admit He gas and adjust its pressure. The pressure of H_2 gas is just the vapor pressure above the solid which can be varied by many orders of magnitude by adjustment of the temperature of the cell from 4.2 K to the boiling point. After trying a number of "reasonable" combinations of He pressure and cell temperature without seeing any unidentified spectra, we abandoned our search for HeH and concentrated on some weak anomalous lines in the 640-nm band of He_2. We then discovered that these features were present, with optimum signal to noise, when helium gas was present in a cell half filled with solid hydrogen at 4.2 K. These features could only be observed when the helium-hydrogen interface was imaged on the monochromator slits. It was under these conditions that the spectra which we attribute to HeH were observed in the 550-nm region. When one realizes that the hydrogen vapor pressure above the solid at 4.2 K is only 6×10^{-7} torr (and 4×10^{-11} torr for D_2)[14] it seems reasonable to conclude that the necessary chemical reactions are taking place adjacent to the solid surface.

Our experimental apparatus, as used for emission spectroscopy, has been previously described.[15] The monochromator employed was a 0.3-m McPherson model 218 and the detector was a cooled EMI 9865B photomultiplier used in photon-counting mode. A newly implemented sample-gas handling system reduced air impurities, described in Ref. 15, below the detector threshold. The experimental method was to admit hydrogen (or deuterium) gas to our 1-cm^3 sample cell at a temperature just below the boiling point and to half fill the cell with liquid. We then cooled the cell to 4.2 K and admitted helium gas to 150 Torr. Excitation of the sample occurred by irradiation with a 15-MeV proton beam, from the McMaster University tandem accelerator, at a current density of 5 nA/cm^2, which entered the cell through a thin Ni window. Radiation was observed at right angles to the proton beam through thin sapphire windows. All of the spectra were taken at 4.2 K with the proton beam turned on.

The spectrum of ^{3}HeD appears in Fig. 1. The transi-

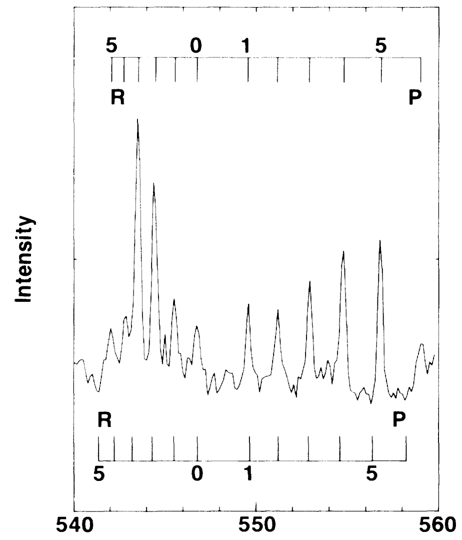

FIG. 1. ^{3}HeD. Top scale shows the predicted wavelengths from the experimental constants of Table I. Bottom scale shows the calculated wavelengths after application of a constant shift of $-364\ \mathrm{cm}^{-1}$.

tion has been identified as the $D\,^2\Sigma^+ \rightarrow A\,^2\Sigma^+$ in the notation of Theodorakopoulos *et al.*[11] This spectrum was taken directly after a survey spectrum from 500 to 750 nm which confirmed the absence of impurities. The spectrum was acquired with use of a fixed dwell time per channel (2 sec) with no attempt to correct for beam-current fluctuations. The observed band is a 0-0 vibrational transition which is consistent with our observations of He_2 and consistent with nested potentials of molecules with similar internuclear separations.

The band clearly has the appearance of a $\Sigma \rightarrow \Sigma$ transition in that the Q branch is missing. Unlike the spectra of Ketterle, Figger, and Walther,[2] no band head is visible because of our lower effective rotational temperature and because the head, for this transition, occurs at a higher J value (>10). All of the transition frequencies (corrected to vacuum) were fitted by a function of the form[16]

$$\nu = \nu_0 + (B_0' + B_0'')m + (B_0' - B_0'')m^2 \qquad (1)$$

with $m = -J$ for the P branch and $m = J+1$ for the R branch; the relevant parameters are collected in Table I. The lines above the spectrum in Fig. 1 are the positions calculated from the experimental parameters and Eq. (1). The lines below the spectrum are those calculated with LeRoy's program and the potential curves of Theodorakopoulos *et al.* Only a constant shift of $-364\ \mathrm{cm}^{-1}$ has been applied to the theoretical numbers which is a correction of 2% to the electronic transition energy. It is our opinion that the data do not warrant any attempt to extract D, the centrifugal distortion term. The same conclusion is drawn with respect to the theoretical potentials since there are only eleven points published for each of them.

The identification of the twelve lines shown in Fig. 1 for ^{3}HeD is unambiguous. Similarly unambiguous is the identification for six lines from ^{4}HeH and nine lines from ^{3}HeH and their parameters are included in Table I. Note the excellent agreement for B'' of the A state with the values of Ketterle, Figger, and Walther[2] of 24.6 cm^{-1} (^{3}HeD) and 36.5 cm^{-1} (^{4}HeH). Further note the near constancy of Δ which is the difference between the experimental and theoretical values of ν_0. Δ is composed mostly of the offset error in the electronic potential curves which is isotope independent. While small mass-dependent contributions could arise from the errors in the shape of the potentials or from the insufficiency of the Born-Oppenheimer approximation, these appear to be smaller than the experimental uncertainties.

Given the ease of identification and the excellent agreement with theory for the spectra for three isotopic combinations, it was surprising to find that the spectrum of ^{4}HeD was not amenable to unambiguous identification, despite the fact that it is the most intense spectrum. Figure 2 shows a plot of this spectrum with tentative rotational identification. The molecular constants, enclosed in parentheses in Table I, are further from the isotope predicted values than expected. All numbering variations that we tried either improved the rotational constant at the expense of the transition energy or vice versa. This spectrum is the only one of the four to show spurious lines, labeled with question marks, in Fig. 2.

Some idea of the self-consistency of the three previously mentioned isotopes and the lack of it for ^{4}HeD can be obtained by comparison of the wavelength differences

TABLE I. Experimental (expt.) and theoretical (theor.) molecular constants for the $D\,^2\Sigma^+ \rightarrow A\,^2\Sigma^+$ transition of HeH. All values in cm^{-1}.

	ν_0 (expt.)	ν_0 (theor.)	Δ	B_0'' (expt.)	B_0'' (theor.)	B_0' (expt.)	B_0' (theor.)
^{3}HeH	18212(3)	18578	−366	38.3(3)	38.9	34.8(3)	36.6
^{4}HeH	18215(4)	18582	−367	36.2(3)	36.5	32.9(3)	34.4
^{3}HeD	18241(2)	18603	−362	24.4(2)	24.5	22.2(2)	23.1
^{4}HeD	18236[a]	18608	−372[a]	23.4[a]	22.1	21.1[a]	20.8

[a] Values perturbed. See text.

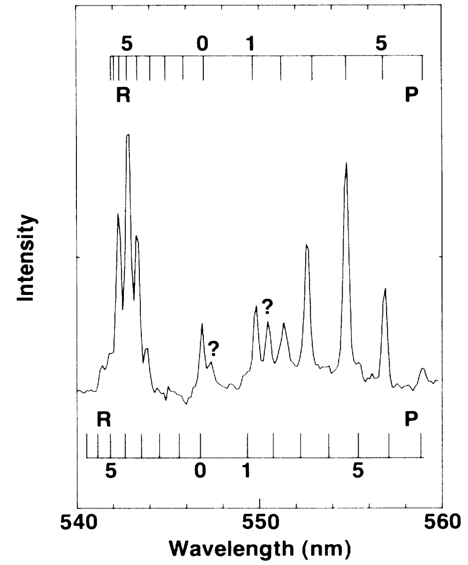

FIG. 2. ^{4}HeD. Scales same as for Fig. 1.

between the measured lines and those predicted by the experimental constants of Table I from Eq. (1). (For the plotted spectra, this is a comparison of the line positions in Figs. 1 and 2 to the upper scale in each figure.) Of the 27 measured lines for ^{3}HeH, ^{4}HeH, and ^{3}HeD, 22 are within 2 cm^{-1} of the predicted values and all lie within 4 cm^{-1}. For the twelve lines of ^{4}HeD, five deviate by more than 4 cm^{-1} and two of these by more than 6 cm^{-1}.

One reasonable explanation for such a perturbation is that a higher vibrational level of the C electronic state is nearly degenerate with the $v=0$ level of the D state. Such an explanation is feasible on the basis of the potential curves of Theodorakopoulos *et al.*[11] Furthermore, such an explanation accounts for the isotope dependence of the perturbation. We have performed calculations on the higher vibrational levels of the C state for both ^{4}HeD and ^{3}HeD. The relevant candidate for perturber has been found to be the $C\,^2\Sigma^+$ $v=3$ level, and we should like to see how close its predicted energy is to that of the $D\,^2\Sigma^+$ $v=0$ level. Only the $J=0$ rotational level will be considered since if a near degeneracy is found for it, a near degeneracy will occur for several of the low-lying J values which is what is needed to explain the observed perturbation.

It is not sufficient to compare just the theoretically obtained energy values when we know that the D and A potential curves have an error in their energy difference of -364 cm^{-1}. We can, however, perform the same analysis for the $C \rightarrow A$ transition, measured by Ketterle, Figger, and Walther,[2] as was performed above in Table I for the $D \rightarrow A$. When that is done we obtain an error of $+113$ cm^{-1} for the energy difference between the C and A potential curves (the same value, within experimental uncertainty, is obtained for both of the published isotopes). Hence the error in the relative energy between the calculated D and C potential curves is -477 cm^{-1}. This number appears to be isotope independent and we need to assume further that it is level independent, at least for the low-lying ($v \leq 3$) vibrational levels. This first-order empirical correction to the energy difference between the D and C potential curves then needs to be added to any theoretical energy difference of interest. Specifically, the theoretical energy difference between the D, $v=0$, $J=0$ level and the C, $v=3$, $J=0$ level is $+481.5$ cm^{-1} for ^{4}HeD. After adding of the correction, the two levels are predicted to lie within 4.5 cm^{-1}. The same two levels for ^{3}HeD, after adding of the same correction factor, are separated by 237 cm^{-1}. We should mention that the $v=3$ levels for the two hydrides (^{3}HeH and ^{4}HeH) have been calculated to be unbound and that no near energetic coincidence occurs with the $v=2$ level for any isotope. Hence our calculation confirms the likelihood of the C, $v=3$ vibrational levels perturbing the D, $v=0$ ones for only the ^{4}HeD isotope.

For such a perturbed level, correct rotational assignments will employ two different R and P sequences from the two interacting vibrational levels making it possible, at least in principle, also to identify the "spurious" lines. A perturbation analysis of the spectrum could then yield the rotational constant of the C, $v=3$ level. Such an analysis is in progress.

Many questions can be raised regarding the excitation method which produced these spectra. This successful method of using helium gas over solid hydrogen was tried near the end of a rather extensive sequence of runs, most of which were performed with He-doped solid hydrogen. Thus matters like the temperature dependence, the gas-liquid interface, and the applicability to rare gas hydrides remain to be investigated.

Some additional information about the location of the reactions could be obtained by lowering of the beam energy. 15-MeV protons pass through 1 cm of solid hydrogen with an energy loss of 8 MeV. But 12-MeV protons cannot make it through the solid and 8-MeV ones will not reach the center of the cell (through the solid).[17] Of course protons at any of these energies readily pass through the helium gas. Such an experiment has not yet been performed.

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