# Preliminary Note

### Direct observation of vibrationally excited hydrogen produced by collisional energy transfer from electronically excited sodium, rubidium, caesium, and mercury

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Hydrogen has been vibrationally excited by direct energy transfer from electronically excited sodium, rubidium and caesium, and mercury. The vibrational excitation of the $B^1\Sigma^+_u \leftarrow X^1\Sigma^+_g$ transitions in hydrogen was detected by absorption of the vacuum u.v. radiation from a low pressure molecular hydrogen lamp.

## Introduction

There has been a continuing interest in the deactivation of electronically excited alkali metals by simple diatomic gases such as nitrogen and hydrogen. As an example, the collisions between electronically excited sodium and ground state hydrogen can be described by the reaction equation:

$$Na(3^2P) + H_2 \rightarrow Na(3^2S) + H_2^v \tag{1}$$

Excess energy is distributed between the translational energy of the products and rotational energy of the vibrationally excited hydrogen $H_2^v$.

There is little direct experimental evidence for reaction (1) except for excited mercury transfer to NO[1], CO[2], and HF[3]. These diatomic molecules were reported to be formed in vibrational levels well below the "resonant" levels, indicating that considerable excess energy was taken up in rotational and translational modes. There are two kinds of indirect evidence for the existence of this process. The large measured quenching cross-section for deactivation of excited sodium atoms by molecular hydrogen[4] and theoretical calculations[5-7] indicated a strong interaction potential between excited alkali atoms and molecular hydrogen.

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The energy distribution of the products of reaction (1) also has been deduced from studies of the reverse reaction[8-12]:

$$Na(3\,^2S) + H_2^v \rightarrow Na(3\,^2P) + H_2 \tag{2}$$

In the most elaborate experiments to date, Fite and coworkers have investigated reaction (2) in crossed-beam experiments[8,9]. A beam of Na atoms at about 650 K was reacted with both $H_2$ and $N_2$, heated from a furnace to temperatures as high as 3000 K, and Na emission was measured. By means of velocity selection, the relative contribution of translational and internal energy in part could be evaluated. A general conclusion which could be drawn from these experiments was that while both kinetic and internal energy were important in reactions of this kind, internal energy plays the more dominant role. The relative contributions of rotational and vibrational energy could not be resolved.

We report here experiments which explore directly both reaction (1) and the reverse process reaction (2). In these experiments, vibrationally excited $H_2$ is produced by collisional energy transfer from electronically excited gaseous metal atoms of Cs, Na, Rb, or Hg. The excited $H_2$ is detected directly by its characteristic absorption in the vacuum ultra-violet.

*Experimental*

Two experiments are described. In the first experiment, which investigates reaction (1), electronically excited alkali or mercury atoms are produced by optical pumping in the presence of hydrogen. Formation of vibrationally excited hydrogen is then observed directly through vacuum u.v. absorption measurements.

The apparatus for the first experiment is shown in Fig. 1. The outer annulus of 1.9 cm o.d. tubing forms a sealed alkali or mercury resonance lamp containing metal vapour in 4 Torr of argon. Metal vapour pressures in that lamp can be controlled by a heater. For Na, Rb, Cs, and Hg, the respective temperatures used were 200, 150, 120, and 20°C. A microwave cavity[13] surrounds the lamp and excites an annular 1 cm i.d. coaxial discharge around the central reaction cell. The reaction cell contains either mercury or alkali metal vaporized with a separate heater. Very slow flow rates of $H_2$ were used at pressures from 0.1 to 700 Torr.
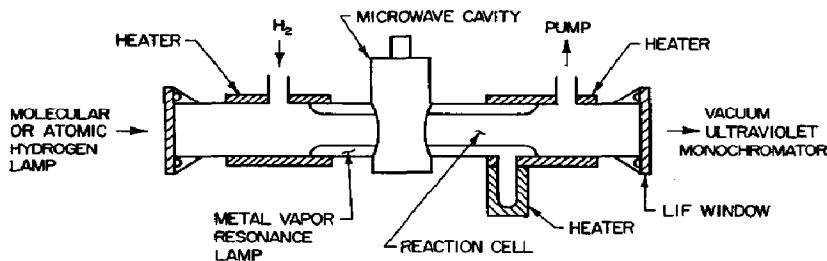


Fig. 1. Schematic diagram of the absorption cell for monitoring $H_2^v$ and H-atoms.

The absorption analysis light source is a molecular hydrogen "resonance" lamp, produced by means of a microwave discharge in a $1\%$ mixture of hydrogen in helium at a total pressure of 2 to 4 Torr. A multitude of vacuum u.v. emission lines are thus generated between the upper $B^1\Sigma^+_u$ state of $H_2$ and the ground $X^1\Sigma^+_g$ state, many of which terminate on higher vibrational levels of the ground state. Suitable portions of the molecular hydrogen emission spectrum are isolated by a 1/4 m Seya–Namioka type vacuum ultra-violet monochromator using equivalent slit widths of 0.1 nm. The absorption of molecular hydrogen at various vibrational levels above the ground electronic state can be detected and measured.

In most of these experiments, only the first excited vibrational level of hydrogen, $(H_2{}^{v=1})$ was measured, the second excited level was observed, and higher levels usually were too weak to be detected. The strongest $v=1$ transitions were in the vicinity of 110 nm and a typical portion of the complex emission spectrum is shown in Fig. 2. This spectrum is a superposition of many rotational lines as shown in Table 1. Only transitions to $v=0$ and $v=1$, however, occur in the region of the spectrum in Fig. 2. Because the lamp is optically thick to $H_2{}^{v=0}$, the absorption signals observed are due only to absorption from $H_2{}^{v=1}$. An absorption technique using a continuum light, rather than a line source, has previously been used to detect the vibrational excitation produced by an electrical discharge in $H_2$[14].

In our experiments, the alkali resonance lamp can be operated continuously, or it can be modulated. A solar blind photomultiplier tube is used as the vacuum u.v. detector. Continuous measurements are made through an electrometer, while sine-varying modulation measurements are made through a pulse-counting train connected to a phase-locked multichannel analyser. The molecular hydrogen absorption source lamp is operated cw. Sensitivities were tested using vibrationally excited hydrogen produced for this purpose in the reaction volume either by electrical discharges or by hot filaments. (We thank J. Flournoy for suggesting this
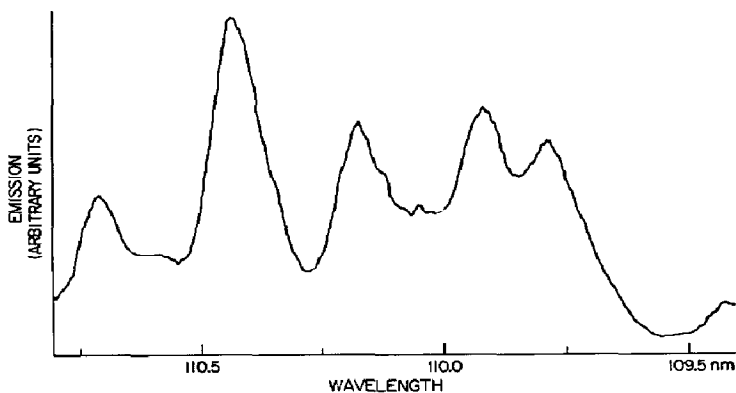


Fig. 2. A small portion of the emission spectrum produced by a microwave discharge of $1\%$ hydrogen in helium. Total pressure 1 Torr.

TABLE 1

ROTATIONAL LINES OF $H_2$ CALCULATED FROM HERZBERG'S CONSTANTS*

| $v', v''$ | $\lambda$ (nm) | $v', v''$ | $\lambda$ (nm) |
|---|---|---|---|
| 5,1 | 109.006 | 5,1 | 109.893 |
| 1,0 | 109.219 | 1,0 | 109.986 |
| 1,0 | 109.272 | 1,0 | 110,022 |
| 5,1 | 109.385 | 4,1 | 110.104 |
| 1,0 | 109.405 | 4,1 | 110.134 |
| 1,0 | 109.423 | 1,0 | 110.427 |
| 5,1 | 109.426 | 4,1 | 110.431 |
| 2,0 | 109.430 | 4,1 | 110.470 |
| 1,0 | 109.645 | 1,0 | 110.473 |
| 1,0 | 109.673 | 0,0 | 110.813 |
| 4,1 | 109.695 | 4,1 | 110.855 |
| 4,1 | 109.747 | 0,0 | 110.863 |
| 4,1 | 109.873 | 4,1 | 110.905 |
| 4,1 | 109.893 | | |

* G. Herzberg, *Molecular Spectra and Molecular Structure*, Van Nostrand, New York, 1950.

technique for producing $H_2^v$.). These tests showed that it was possible to monitor both the $v=1$ and $v=2$ levels of $H_2$.

A second apparatus was constructed to investigate reaction (2); this apparatus was similar to the first except that provision was made for adding a second alkali metal vapour to the reaction volume. Evidence for the transfer of vibrational energy from $H_2$ was sought by looking for fluorescence from the second alkali metal. For example, Na vapour in the reaction cell and excited by means of external resonance radiation, is capable of transferring sufficient energy to excite $H_2$ into vibrational levels up to $v=4$. If Cs is also present, transfer of vibrational energy from $v=3$ or 4 of $H_2$ can excite Cs to the $6^2 P$ state resulting in Cs emission at 852.1 and 894.3 nm. Figure 3 illustrates this double resonance apparatus. Vapour pressures of Na are controlled both in the resonance lamp and in the cell by adjusting the separate furnace temperatures. A maximum Na fluorescence signal at 589 nm in the direction of the monochromator determines optimum operating conditions. Molecular hydrogen is added so that half of the observed
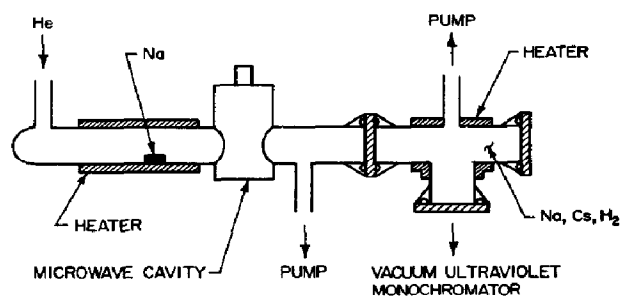


Fig. 3. Schematic diagram for a double resonance experiment to measure energy transfer from Na* → $H_2^v$ → Cs*.

fluorescence is quenched. The vapour pressure of the Cs used must also be separately controlled. The Cs fluorescence near 850 nm is isolated through a monochromators detected with a red-sensitive photomultiplier tube.

*Results*

Using the apparatus shown in Fig. 1, strong (as much as 30%) cw absorption was observed for the first excited vibrational level of hydrogen $H_2{}^{v=1}$ produced by excitation from Na, Rb, Cs, and Hg. The second vibrational level was weakly detected; levels higher than the second level were not detected, indicating possible rapid relaxation of higher vibrational levels to the first level. These experiments constitute direct evidence for reaction (1). Surprisingly, mercury, which is in a separate category from the alkalis, also produces vibrationally excited hydrogen. Recent work by Callear[15] indicates that a major primary process for the reaction of electronically excited mercury with hydrogen first produces HgH:

$$Hg(^3P_1) + H_2 \rightarrow HgH + H \tag{3}$$

Thus, it was possible that the vibrationally excited hydrogen we observed could arise from the secondary process

$$H + HgH \rightarrow H_2{}^{v} + Hg. \tag{4}$$

Monitoring the time history of both H atoms and $H_2{}^{v}$ indicates, however, that this is not the case. We find that significant amounts of vibrationally excited hydrogen can be produced from Hg excitation in a process analogous to reaction (1). These Hg experiments will be described in detail elsewhere[16].

In contrast to the mercury reaction, the alkali metal reactions are insufficiently energetic for a single step process to produce a hydrogen atom and the alkali hydride. Other secondary processes conceivably could produce such H atoms, but this possibility was shown to be unimportant. With an optically-thin hydrogen atom resonance-lamp, no absorption was observed at 121.6 nm, the position of the strong Lyman-$\alpha$ line of H.

We also tried to characterize the distribution of the vibrationally excited hydrogen produced from reaction (1). To improve detection sensitivity, the alkali metal resonance lamp was modulated. In this way, the $v=2$ level was weakly but clearly observed; levels higher than the second were not detected. Detectability limits were about 0.2%. Figure 4(a) shows $H_2{}^{v=1}$ relaxation from the square wave-modulated production from Cs. The $v=2$ level, observed at an intensity roughly tenfold weaker than $v=1$, parallels the decay of the $v=1$ level. This indicates that equilibration has already occurred within the 100 $\mu$s time resolution of the apparatus. Thus, relaxation by vibrational interchange is apparently faster than 100 $\mu$s.

In contrast, for the case of Hg sensitization at 253.7 nm, there was evidence for decay from upper levels. Because of the considerably larger amount of energy available, $H_2$ can be populated to vibrational levels as high as $v=13$. For the $v=1$
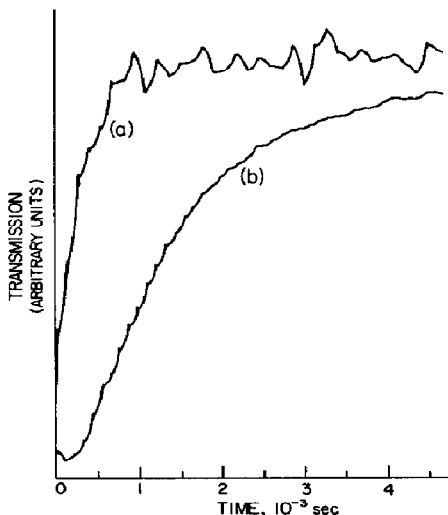
Fig. 4. Plot of transmission through the reaction cell of $v=1$ emission lines at 109.7 nm from a molecular hydrogen resonance lamp. (a) $H_2^v$ produced by collision with $Cs^*$; maximum absorption is about 10%. (b) $H_2^v$ produced by collision with $Hg^*$; maximum absorption is about 15%. An induction period can be observed during the first several hundred µs.

level of $H_2$ produced by Hg excitation, an induction period lasting roughly several hundred microseconds can be clearly observed. This induction period is illustrated in Fig. 4(b) for a total $H_2$ pressure of several Torr. At higher $H_2$ pressures, the induction period can be totally eliminated. From this induction period, the rate constant for deactivation of upper levels was calculated to be approximately $10^{-13}$ $cm^3$ $molecule^{-1}$ $s^{-1}$, corresponding to a deactivation efficiency of about $10^{-4}$. This value is of comparable magnitude to that observed[17] for deactivation of vibrationally excited CO.

Experiments designed to investigate reaction (2), the transfer of energy from excited Na to hydrogen and thence from vibrationally excited hydrogen to Cs, resulted in a barely discernible signal. The Cs fluorescence was approximately $10^{-4}$ of the Na fluorescence signal.

*Discussion*

From our time-resolved experiments in which the formation and decay of vibrationally excited hydrogen is monitored, a conclusion can be formed about the mechanism for relaxation of the first excited vibrational level. Vibration-vibration collisional transfer degrades all higher vibrational levels to the first level. Ultimately, there must be transfer from the first level to the ground level either by vibration–translation exchange or by deactivation through collisions with the wall. Figure 4 shows that the relaxation times for $v=1$ are roughly (though not exactly) comparable in the Hg and Cs systems. Relaxation of $H_2^{v=1} \rightarrow H_2^{v=0}$

was found to be independent of $H_2$ pressure and of light intensity. The relaxation followed first order kinetics. Addition of several hundred Torr pressure of inert gas sufficiently lengthened the diffusion time to eliminate wall deactivation as the relaxation mechanism. We therefore conjecture that deactivation from the first vibrational level occurs through collision with mercury or with the alkali metal. This rather surprising conclusion indicates a strong interaction between the alkali metal and hydrogen with an estimated deactivation probability of the order of $10^{-1}$ to $10^{-2}$. The deactivation measured here is significantly faster than the wall deactivation rates measured for the $v=1$ level produced by microwave excitation of hydrogen[14].

Transfer of electronic energy from excited alkalis and mercury to hydrogen was observed directly by spectroscopically monitoring $H_2{}^{v=1}$. Of the states higher than $v=1$, only $v=2$ could be detected. With mercury, relaxation from upper levels was indirectly observed through observation of an induction period in the $v=1$ level from which the efficiency of deactivation from upper levels to $v=1$ was calculated to be about $10^{-4}$. The distribution of vibrationally excited hydrogen could not be determined with the sensitivity and time resolution of the present apparatus.

Attempts to characterize the vibrational distribution by means of excitation by one alkali metal and detection by another did not produce useful results using the present apparatus. This is almost certainly due to a limitation in sensitivity because subsequent experiments were successful[18] when the monochromator was replaced with suitable filters, and the sodium resonance lamp was replaced with a tunable dye laser.

The capability of producing specific vibrational states of a diatomic molecule by energy transfer from one alkali metal and the specific detection of these states by energy transfer to a second alkali metal of lower energy should provide a very sensitive means for monitoring specific vibrational states and for evaluating their energy exchange processes.

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