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Vibrational relaxation of hydrogen by direct detection of electronic and vibrational energy transfer with alkali metals*

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A technique has been developed to measure the rate constant for vibrational relaxation of $H_2^{v=3,4}$ by $H_2^{v=0}$. The technique uses a mechanically chopped, tunable, cw dye laser coincident with either of the Na resonance lines at 589.6 or 589.0 nm. Sodium vapor is contained in a glass cell along with Cs atoms and H_2. Sodium atoms, excited by the dye laser radiation, collisionally transfer electronic energy to H_2 producing some H_2^v. Only vibrational energy in H_2^v from levels $v = 3,4$ can transfer to Cs as electronic energy and cause Cs resonance line emission at 894 and 852 nm. In this manner, using the observed emission as a detector of $H_2^{v=3,4}$, the vibrational relaxation rate constant was determined to be 3.9×10^{-14} cm^3 sec^{-1}. Similar rate constants were measured, with somewhat less accuracy, for D_2^v colliding with D_2 and for H_2^v colliding with He. It was found that N_2, Na, and Cs also undergo electronic to vibration and vibration to electronic energy exchange.

INTRODUCTION

There has been considerable work on transfer of internal energy from diatomic molecules to electronic energy in sodium.[1-5] As an illustration of processes of this kind it has been suggested that energy transfer from vibrationally excited nitrogen to sodium is responsible for the sodium emission in the aurora.[6] The inverse process, electronic to vibrational transfer, has been observed for the transfer of electronic energy in Hg atoms to vibrational energy in diatomic CO, NO, and HF,[7-10] but it has only recently been directly observed for alkalis and diatomics.[11] Large measured quenching cross sections for the deactivation of sodium atoms by molecular hydrogen and nitrogen[12] and theoretical calculations demonstrating the existence of a strong interaction potential between alkali atoms and these diatomics[13-15] have lent indirect support to the premise of the occurrence of electronic to vibrational energy transfer. This paper describes a technique for experimentally observing both processes, electronic to vibration and vibration to electronic. Using this technique the rate constant k_1 for the reaction

$$H_2^{v=3,4} + H_2^{v=0} \rightarrow H_2^{v\leq 3} + H_2^{v=1} \qquad (1)$$

was measured.

A summary of the technique is as follows: These measurements require a source of H_2^v and a detector of H_2^v. A monochromatic light source, a tunable dye laser, is used to excite Na atoms at 589.0 or 589.6 nm in a vapor cell which also contains H_2 and Cs atoms. Electronically excited Na atoms collisionally transfer energy to vibrational energy in the H_2 molecules $H_2^{v\leq 4}$. The $H_2^{v=3,4}$ collisionally transfer some vibrational energy to electronic excitation of Cs ($6^2P_{1/2,3/2}$). Electronically excited Cs atoms radiate at the resonance wavelengths, 894 and 852 nm. The dye laser is pulsed, i.e., chopped, and at the end of the excitation pulse there is a resultant concentration of vibrationally excited H_2, $[H_2^{v\leq 4}]$. The vibrationally excited H_2, $[H_2^{v=3,4}]$, which can transfer to Cs can also be quenched by ground state H_2. In the experiments here, the decay with time of Cs ($6^2P_{1/2,3/2}$) fluorescence is due primarily to vibrational relaxation of $H_2^{v=3,4}$ by $H_2^{v=0}$ through Reaction 1.

EXPERIMENTAL

A block diagram of the experimental arrangement is shown in Fig. 1. A cw dye laser similar in design to that described by Ippen *et al.*[16] was used to excite the Na atoms. Since the Doppler linewidth of Na is about 3 GHz, a 1.5 mm solid etalon (30% reflectivity) was placed in the dye laser to achieve a sufficiently narrow bandwidth and also to give a fine wavelength tuning control. With the etalon, there were two longitudinal cavity modes of equal intensity separated by 1.2 GHz and at a total power near 100 mW.

Pulses of the dye laser radiation were generated by directing the laser beam through a two-hole mechanical chopper, rotating at 450 Hz, placed at the focus of a 5 cm focal length lens. The laser

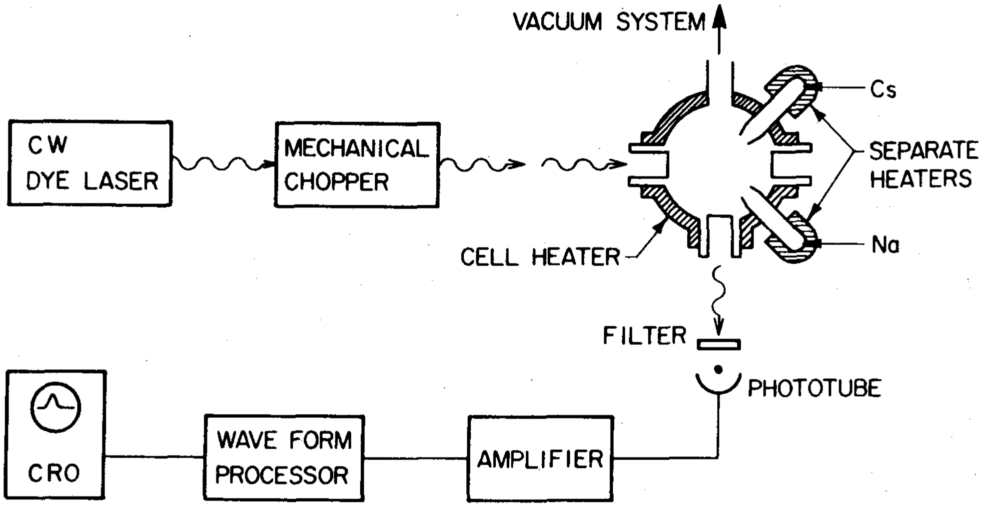

FIG. 1. A block diagram of the apparatus showing the excitation, detection, and signal processing.

beam was then recollimated by a 14 cm focal length lens. Pulses were thus generated at a rate of 10^3 sec^{-1} with a width of 50 μsec and a 1 μsec rise- and falltime. This pulsed radiation was directed through the alkali vapor cell.

The quartz alkali vapor cell was 6 cm in diameter with four observation ports. Windows of the observation ports were recessed so as not to be cold areas of the cell. Independent temperature control of the cell body, cell window ports, Na reservoir, and Cs reservoir was achieved by the use of separate heaters. Typical operating temperature for the cell body and window ports was 200 °C; the Cs reservoir was operated at 90 °C. The Na reservoir was activated once (200 °C) at the beginning of the experiment and from then on remained cold (1 week). Absorption measurements indicated that the Na pressure was approximately 5.5×10^{-7} torr. Since the vacuum line to the pumping station was cold (i.e., room temperature), the cell operated in a nonthermal steady state condition. It was found that the addition of 5–10 torr of He gave a more uniform temperature distribution inside the cell, and hence all measurements were made with some He present (normally 5 torr). The vapor pressure of Cs was not more than 3×10^{-4} torr, corresponding to 90 °C, and was most likely considerably less due to the nonequilibrium nature of the cell. No absorption measurement was made to determine the Cs pressure.

Cesium resonance radiation was detected at 90° from the dye laser beam by a red sensitive photomultiplier tube. A small amount of fluorescence from two filters, used to eliminate the Na resonance radiation, gave weak signals which followed the time evolution of the excitation pulse even in the absence of H_2. This background signal was helpful in checking the electronic system. The output of the photomultiplier tube was terminated in a 10 kohm resistor and fed into an amplifier, which was the vertical amplifier of two oscilloscopes connected in series. The output of the amplifier was fed into a transient waveform integrator and displayed on an oscilloscope. Photographs were then taken of the resulting waveform. The system response was checked by detecting the Na fluorescence with a different optical filter and through suitable attenuation. An illustration of the system response for Na is shown in Fig. 2(a). Figure 2(b) shows the Cs resonance emission signal at a H_2 pressure of 10 torr. The maximum Cs

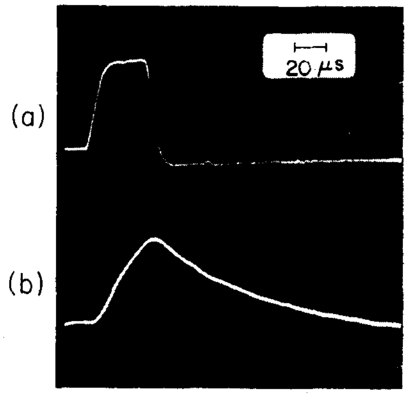

FIG. 2. Typical signals after being processed by the transient waveform integrator. These traces represent an integration of about 10^4 pulses. The Na resonance emission with a 5 μsec rise- and falltime and 50 μsec width is shown in trace *a* for comparison with trace *b*, the Cs resonance emission with 10 torr pressure of H_2 in the vapor cell.

emission signals were about 10^{-5} of the direct Na fluorescence signals.

RESULTS

If Na and Cs have a negligible effect on the deactivation of H_2^v, the time rate of change of $[H_2^{v=3,4}]$ may be written in differential form as

$$(\partial/\partial t)[H_2^{v=3,4}] = -k_1[H_2^{v=3,4}][H_2] ,$$

with a solution of

$$[H_2^{v=3,4}] = [H_2^{v=3,4}]_{t=0}\exp(-t/\tau) ,$$

where t is measured from the end of the laser excitation pulse and where $\tau^{-1} = k_1[H_2]$. The Cs radiation is proportional to $[H_2^{v=3,4}]$ and has the same mathematical form and the same time constant τ. Therefore, the rate constant k_1 can be determined from a measurement of τ and H_2 pressure. In the above equations we specify both the third and fourth vibrational levels, although for clarity it should be noted that if both $H_2^{v=3}$ and $H_2^{v=4}$ transfer vibrational energy equally effectively to the Cs tracer, then the rate of relaxation that we actually measure is only for $H_2^{v=3}$, since the fourth vibrational level must ultimately funnel into the third via v–v transfer (Reaction 1). If on the other hand, $H_2^{v=3}$, which has a very close energy match with the Cs (6^2P) state, does not efficiently transfer energy to Cs, then the relaxation rate that we measure is only for $H_2^{v=4}$. Although the former possibility is the more likely, we employ the more general and less specific notation for the relaxation process as occurring from both states i.e., $H_2^{v=3,4}$

Measured time constants τ of the Cs resonance radiation were obtained for H_2 pressures from 5–50 torr. Reciprocals of τ were plotted against H_2 pressure. Figure 3 shows the expected linear relation between τ and H_2 pressure. Measured time constants were found to be independent of both sodium and cesium pressures, although the signal strengths did markedly vary with change of these parameters. The value of k_1 determined from these data is $k_1 = 3.9\ (\pm 0.4)\times 10^{-14}\ \mathrm{cm^3\ sec^{-1}}$.

Deuterium was employed in similar, although less detailed experiments for the purpose of establishing whether signal strengths comparable to those from H_2 could be obtained from D_2. While electronically excited sodium can vibrationally excite hydrogen up to the fourth level, D_2 can be excited up to the sixth level. The third and fourth vibrational levels in H_2 can electronically excite Cs while the fifth and sixth vibrational levels in D_2 are involved. Emission signals from excited Cs obtained from D_2 were about a factor of 2 weaker than those from H_2 under otherwise identical experimental conditions. Similarly for D_2 the relaxation

$$D_2^{v=5,6} + D_2^{v=0} \rightarrow D_2^{v\leq 5} + D_2^{v=1} \qquad (2)$$

was measured. The rate constant k_2 obtained from Fig. 3 was found to be $k_2 = 4.9\ (\pm 1.5)\times 10^{-14}\ \mathrm{cm^3}$ $\mathrm{sec^{-1}}$.

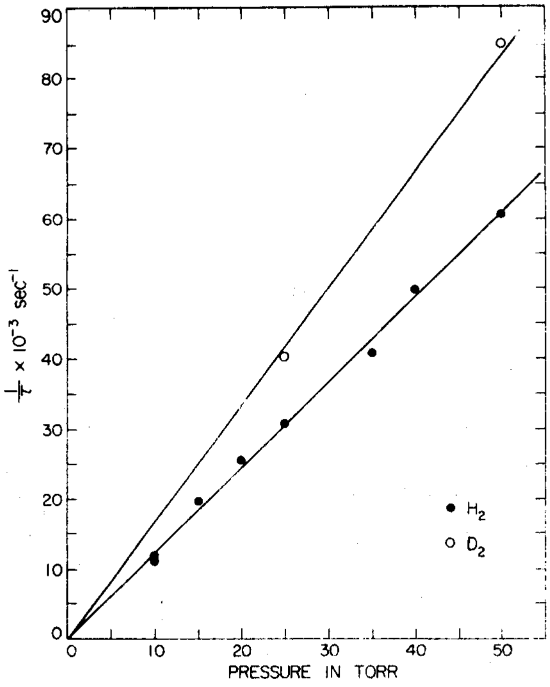

FIG. 3. A plot of τ^{-1} vs H_2 pressure showing the expected linear dependence.

The relaxation rate of H_2^v by collisions with He. (3) also was estimated with the result of $k_3 < 2 \times 10^{-15}\ \mathrm{cm^3\ sec^{-1}}$.

$$H_2^{v=3,4} + \mathrm{He} \xrightarrow{k_3} H_2^{v\leq 3} + \mathrm{He} . \qquad (3)$$

Similar experiments with nitrogen demonstrated that N_2, Na, and Cs also participate in electronic to vibration and vibration to electronic energy transfer. Signal strengths, however, were about 10 to 15 times weaker than for H_2, and reliable relaxation rates were not obtained.

CONCLUSION

A technique for measuring vibrational relaxation rates has been described and its usefulness demonstrated. The signals observed in these experiments can be improved by several orders of magnitude. Various combinations of alkali metals and reactant molecules may be used to measure vibrational relaxation rates which are difficult or impossible to measure by other methods.[17] These experiments also demonstrate the applicability to detecting the transfer of electronic energy to vibrational energy and also the transfer of vibrational energy to electronic energy of alkali metals and simple diatomic molecules. A refinement of the present experimental technique should allow a direct determination of a number of these cross sections. The technique may perhaps be applied to cross transfer between alkali metal spin doublets through vibrational energy transfer rather than by direct spin-orbit relaxation.

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