

Inelastic and reactive collisions of Cs($9^2P_{3/2}$) with hydrocarbons

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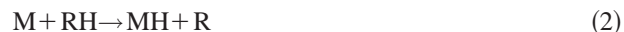
Cs atoms when excited to their 7^2P , 8^2P , and 9^2P states have sufficient internal energy to be able to react with H_2 molecules forming CsH and H and they do so. Cs 9^2P has sufficient energy to react with alkanes; in fact, this does not occur. Instead an efficient n changing but l conserving collision occurs producing Cs atoms in the lower 2P states. This phenomenon is shown to result from the fact that in the Rydberg state the valence electron is remote from the Cs^+ ion core. Cs 9^2P does react with propene removing an allylic H atom to form CsH. © 2002 American Institute of Physics.
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INTRODUCTION

The reactions of electronically excited atoms with molecules is an old subject.¹⁻⁴ Formerly the excitation of atoms was used as an adjunct to photochemistry. In a process called photosensitization energy was transferred indirectly to a molecule *via* an atom rather than directly. The photon energy derived from an atomic resonance lamp converted the atom from a nonreactive to a reactive species. For example, the reaction



is exothermic but the reaction



is endothermic. In these equations M is a metal atom and RH is a nonmetallic hydride.

The introduction of lasers has altered this old subject drastically. Because laser light is so intense almost any allowed transition can be effected. Parity forbidden transitions can be effected by a two photon transition. Most important, the product MH can be probed by laser induced fluorescence. Thus reactions of the form of Eq. (1) have become an interesting field of chemical dynamics.

The most commonly used atoms have been the divalent atoms, zinc, cadmium, and mercury because of their (a) relatively high vapor pressure at temperatures not much above room temperature, (b) nonreactivity in the ground state, and (c) relatively high resonance energies. Breckenridge and co-workers have built a substantial body of knowledge of the reactions of atoms $M(nsnp)$ with H_2 , CH_4 , and SiH_4 .⁴ Their central conclusion is that the reaction takes place *via* an insertion. The complex thus formed bends and then dissociates forming a rotationally excited but vibrationally cold MH product. The lack of vibrational excitation was explained as a late release of product from an RMH complex in which the M-H distance is similar to that in free MH. In practice H_2 and SiH_4 reacted easily but CH_4 did not. H_2 offers no steric barrier to a sidewise attack. SiH_4 may have a lower steric

barrier to insertion because the Si-H bond distance of ~ 1.5 Å is much longer than the 1.1 Å C-H bond length.

In contrast to the very extensive research carried out on the reactions of excited divalent atoms, there have been few reports on the reactions of excited alkali atoms. Those that have appeared describe reactions of various excited states of Na, K, and Cs with H_2 .⁵⁻⁸ There have been no reports of reactions of excited alkali atoms with hydrocarbons. This paper describes attempts, all but one unsuccessful, to detect the CsH product of the reaction



EXPERIMENT

The heart of the apparatus was a series of 2.5 cm diameter Pyrex tubes joined together at various points. The cesium contained in a glass ampule with a break seal was at the bottom of a 40 cm long vertical tube. At 30 cm up there was a 10 cm horizontal side tube directed towards a photomultiplier tube (PMT). In the opposite direction there was still another horizontal tube terminating in a glass to metal seal and a 2.75 in. Conflat flange. The system was closed with a butterfly valve with 2.75 in. Conflat flanges on each side. This tube contained a small depression in which a short iron rod was placed. At the start of the experiments, after evacuation, the piece of iron was moved with an external magnet and fell down the vertical tube breaking the ampule. Perpendicular to this tube was a 60 cm tube attached at its middle to the vertical tube. At one end a quartz window was sealed and at the other end a Pyrex window. These windows, set approximately at Brewster's angle were for the 361 nm pump and 500-540 nm probe lights, respectively. The PMT was a Hamamatsu R943-02 chosen because of its high sensitivity in the red and near IR. To vaporize the cesium the lower part of the vertical tube was wrapped with electrical heating tape. The upper part of this tube and the tube leading to the PMT were wrapped with a separate heating tape. The upper tape was heated to about 165 °C, somewhat hotter than the lower tube to prevent condensation of Cs on the windows.

The 361.2 nm light used to excite Cs was generated by frequency doubling using an Inrad Autotracker a fundamental wavelength of 722.4 nm, the output of a YAG pumped

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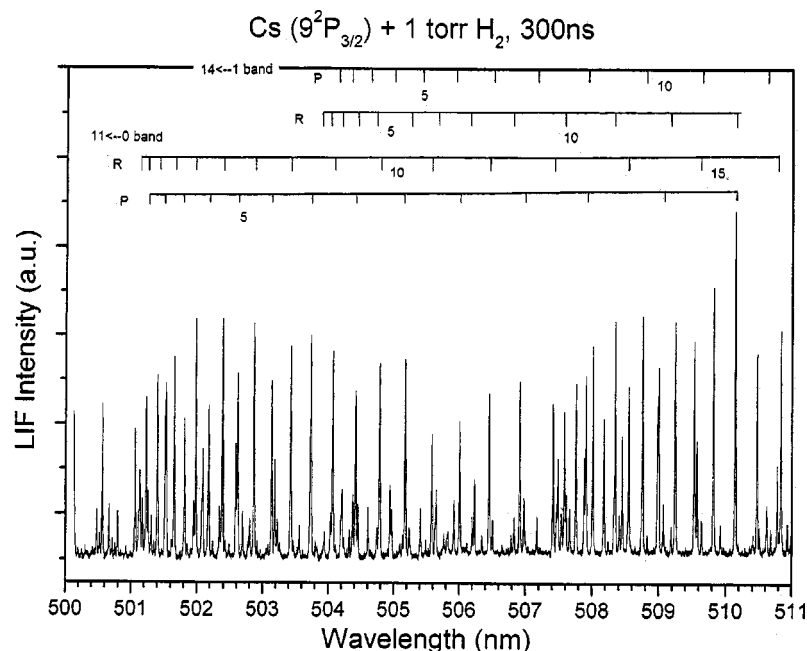


FIG. 1. The LIF excitation spectrum of the CsH product of the reaction between Cs $9^2P_{3/2}$ and H_2 (1 Torr) taken 300 ns after the 361.25 nm excitation pulse. Three bands (11,0), (10,0), and (14,1) are overlapped.

dye laser. A band pass filter located at the exit of the Autotracker removed the 722.4 nm light but passed the pump beam. The probing laser light extending from 500 to 540 nm was made by pumping Coumarin 500 by a Lambda Physik Scanmate dye laser with the 150 mJ third harmonic of a Continuum Powerlite YAG laser. The probing light was weakened with a neutral density filter. A band pass filter transmitting light mainly at $\lambda > 600$ nm was used to remove scattered light from both the pump and probe lasers. The pump and probe dye lasers were pumped by separate YAG lasers. The delay between the pump and probe was controlled by a Stanford Research Digital Delay Generator.

RESULTS

Figure 1 shows the fluorescence excitation spectrum of the CsH product of the reaction of Cs($9^2P_{3/2}$) with H_2 . The large numbers of lines $X^1\Sigma(v''J'') \rightarrow A^1\Sigma(v'J')$ observed are partly due to the fact that the vibrational frequency in the A state is small, 166 cm^{-1} and partly to the warm but not hot rotational distribution. From 500 to 540 nm lines of the (11,0), (10,0), (9,0), (8,0) and (14,1), (13,1), (12,1), etc., are observed. The spectrum shown contains lines of the (11,0), (14,1) and, after 507 nm also the (10,0) band originating from different rotational states. The signal/noise is considerably improved over that found in an earlier experiment.⁸ (Compare Fig. 1 with Fig. 3 of Ref. 8.) The original conclusions remain the same. There is only minor vibrational excitation and low rotational energy. In the previous work on the reaction of Cs 9^2P with H_2 it was found that the LIF excitation spectrum taken at a delay time of 300 ns in the presence of 0.7 Torr of H_2 was indistinguishable from that taken with 1 Torr of H_2 . In the present experiments it was found that the LIF excitation spectrum taken at a delay of 300 ns was indistinguishable from that taken at a delay time of 200 ns. The \ln of the intensities of lines originating from the state $v''=0$ and rotational quantum number J are plotted against

$J(J+1)$ in Fig. 2. A similar logarithmic plot of intensities of lines originating from the $v''=1$ state is also in Fig. 2. Only one very weak line was found originating from the $v''=2$ state. The straight lines which fit these logarithmic plots show that the rotational distributions have the Boltzmann shape and give the rotational temperatures and relative yields of the $v''=0$ and 1 states shown in Table I. The population ratios of the $v''=1$ and 0 states were taken to be the ratios of the intensities of the transitions $(v',1)$ and $(v',0)$. The Franck-Condon factors were not included because the transitions were saturated.

A series of experiments was carried out in which the reactant hydrogen was replaced with methane, ethane, propane, cyclopropane, and cyclohexane. There were no lines observed due to CsH. Instead there appeared a strong spectrum, shown in Fig. 3 which was completely different from that of CsH. It turned out to be a series of transitions to 2S and 2D Rydberg states originating from the $6^2P_{3/2}$ and $6^2P_{1/2}$ levels. The energy level diagram of Fig. 4 shows some of the transitions observed. The signal intensity was measured as a function of time and pressure to determine the mechanism of formation of the 6^2P Cs atoms.

After exciting Cs atoms with 361 nm light a fluorescence decay can be observed. This decay is greatly accelerated on addition of a vapor of a hydrocarbon. Figure 5 is a plot of the decay rate of the fluorescence as a function of methane pressure. Each of the five points in the plot were derived from a logarithmic plot of the decay intensity versus time at a given methane pressure. Inspection of the v^3 factors for the various

TABLE I. Rotational temperatures and vibrational population ratios.

Reaction	$T_R(v''=0)$	$T_R(v''=1)$	$P(v''=1)/P(v''=0)$
Cs($9^2P_{3/2}$)+ H_2	433 ± 21 K	405 ± 45 K	0.11
Cs($9^2P_{3/2}$)+ $CH_3CH=CH_2$	559 ± 34 K	371 ± 4 K	0.13

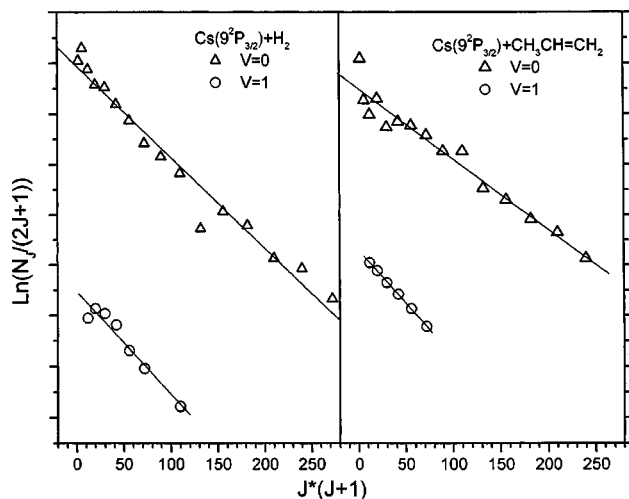


FIG. 2. $\ln(N_j/(2J+1))$ vs $J(J+1)$ for the (11,0) and (14,1) bands of CsH products of the reactions of Cs $9^2P_{3/2}$ with hydrogen and propene.

transitions suggests that most atoms decay to the ground 6^2S state. The rate constant for the quenching process, derived from the slope is $(2.21 \pm 0.07) \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ which means that the average cross section for a Cs- CH_4 quenching collision is about 30 \AA^2 . The radiative rate constant cannot be determined accurately from this plot but in separate measurements it has been found to be $5 \times 10^6 \text{ s}^{-1}$.

After its formation the Cs(9^2P) can only decay. However, the populations of the lower energy 6^2P states start from a very small value, rise to a maximum and then fall. Typical curves are shown in Fig. 6. The fact that there is a signal even in the absence of a hydrocarbon molecule means that there is a small probability of a two photon cascade from $9p$ to $6p$ via an s or d state. The rise and fall were fitted with a growth rate constant of $(1.83 \pm 0.06) \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ and a decay rate which was the reciprocal of the fluorescence lifetime. The fact that the growth rate is linear in the methane pressure (see Fig. 7) means that only one collision was required for the $9p$ to $6p$ transition. The fluorescence lifetime of a Cs atom in the $6^2P_{3/2}$ state is

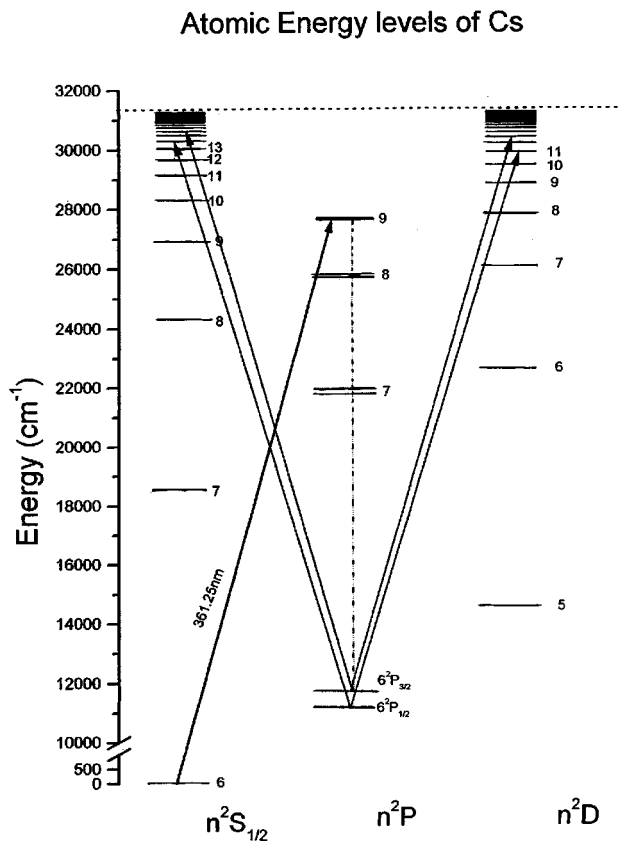


FIG. 4. Energy level diagram of the Cs atom. The initial excitation is shown as an arrow starting from the $6s$ state. The inelastic transition during a collision is shown by the dotted lines. The LIF transitions to Rydberg states are indicated by the diagonal arrows originating in the $6p$ states.

$32.7 \pm 1.5 \text{ ns}$.¹⁰ This very fast decay is faster than the collision rate at most of the pressures used in these experiments so that the decay rate was taken to be equal to the radiative rate.

Believing that the weaker the C-H bond the more likely would be a reaction, the vapor of 1,3,5-cycloheptatriene (CHT) was introduced into the system but the Cs atom fluo-

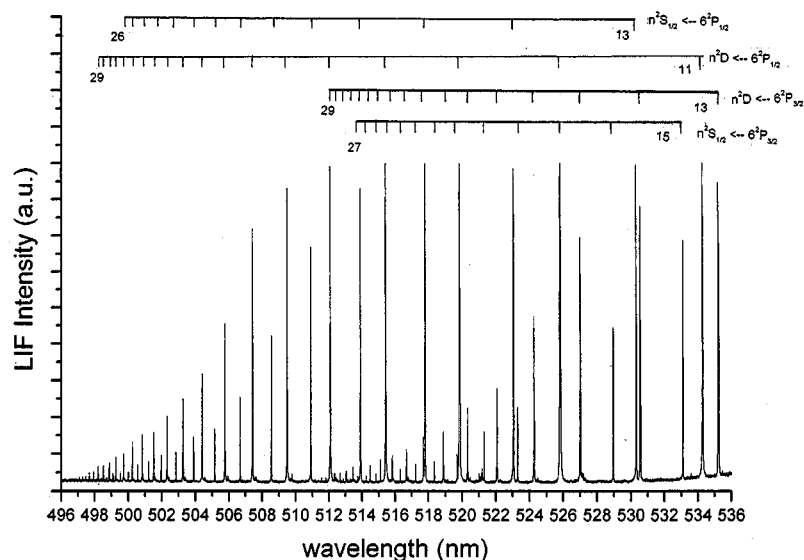


FIG. 3. LIF excitation spectra of Cs $6^2P_{3/2}$ and Cs $6^2P_{1/2}$ formed by collision of methane with Cs $9^2P_{3/2}$. Spectra were taken 300 ns after the 361.25 nm exciting pulse. In order to make the weaker transitions visible some of the stronger lines have been truncated.

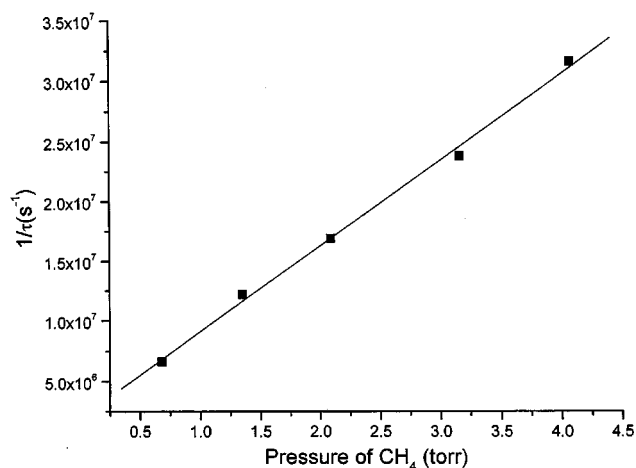


FIG. 5. Rate of decay of fluorescence from Cs $9^2P_{3/2}$ vs pressure of methane. The slope of the linear plot yields a rate constant of $2.21 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ for decay of the population in the $9^2P_{3/2}$ state.

rescence disappeared at once. A possible explanation is that the CHT has sufficient electron affinity that a salt Cs^+CHT^- was formed. The phenomenon was not investigated further. A less exotic molecule with a relatively weak C–H bond is propene, $\text{CH}_3\text{CH}=\text{CH}_2$. It did not react with ground state cesium but did with the electronically excited cesium producing CsH in lower yield than with hydrogen but with a similar rovibrational state distribution. The LIF excitation spectrum is shown in Fig. 8 and the \ln of the intensities of

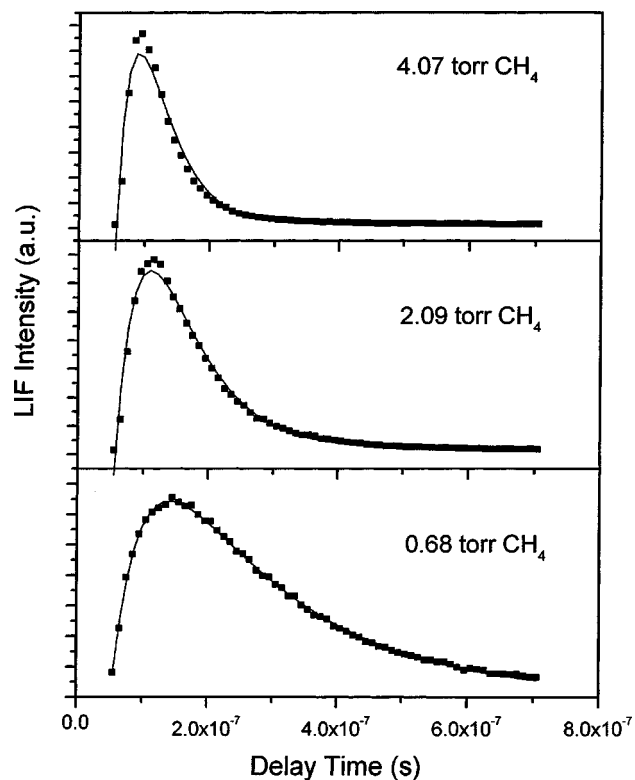


FIG. 6. LIF excitation intensity of the Cs $6^2P_{3/2} \rightarrow 17^2S_{1/2}$ vs time at three different pressures of methane. These curves and curves at two other pressures were fitted with a sum of two decaying exponentials $C(\exp(-t/\tau) - \exp(-t/\tau_0))$ where τ_0 is 32.7 ns, the fluorescence lifetime of the $6^2P_{3/2}$ state.

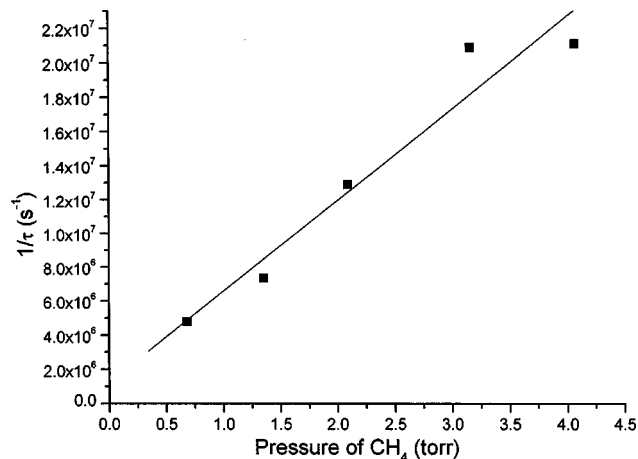


FIG. 7. $1/\tau$ as determined from the curves of Fig. 6 is plotted against the methane pressure. The slope yields a second order rate constant of $1.83 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$.

the lines versus $J(J+1)$ is plotted in Fig. 2. The rotational temperatures and relative vibrational populations derived from the plots are in Table I.

DISCUSSION

Reactive collisions

The data in Table I show that the CsH product of the reactions of Cs($9^2P_{3/2}$) with hydrogen and propene are evidently very similar. Nevertheless, as shown in Table II, there is far more available energy in the reaction with propene. Our first puzzle is that there seems to be little or no activation energy in the reaction with hydrogen but a large activation energy in the reactions with alkanes, acyclic, and cyclic. Similar results were observed in the reactions of M(nsnp) with hydrogen and alkanes.⁴ In that case the large activation energy was ascribed by Breckenridge to steric hindrance opposing the insertion of a metal atom. The mechanism of insertion is very natural with divalent metal atoms, M because of the existence of the compounds CH_3MCH_3 . There are no such compounds of the univalent alkali metals.

The vibrational distribution is very similar to what was observed for the divalent atoms' reactions, i.e., almost 90% of the product MH are produced in the $v''=0$ state irrespective of the amount of available energy. This is a strong indication of a late reaction barrier in which in the transition state the M–H distance is very close to that of the free MH molecule. However, one could have a late barrier with an insertion or an abstraction mechanism. Moreover, the 9^2P state of cesium is different from the (nsnp) states of Zn, Cd, and Hg. The Cs state is only 0.38 eV below the ionization potential of Cs whereas, for example, the 3P_1 state of Hg is 5.54 eV below its ionization potential. The Cs atom is truly in a Rydberg state in which the electron is typically remote from the Cs^+ core. In the $9p$ state of a hydrogen atom the peak of the wave function is at 81 Bohr radii. The Cs $9p$ wave function is not that diffused but is very extended. The collision can be envisioned as a collision of a Cs^+ ion with a molecule during which the greatly extended charge distribution of the $9p$ electron collapses. The system passes from a

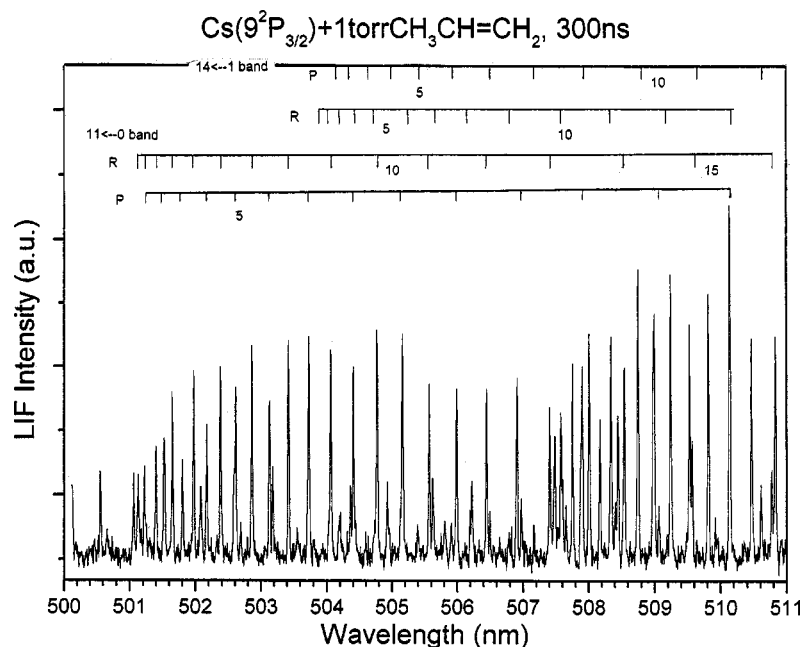


FIG. 8. The LIF excitation spectrum of the CsH product of the reaction of Cs $9^2P_{3/2}$ with propene. Note the close similarity of the spectrum of Fig. 1 taken at the same pressure and delay time.

stable deep well, $\text{Cs}^+\text{-RH}$ to a strongly repulsive surface. The Cs^+ ion strongly attracts the polarizable molecule and holds it at a short distance. The neutral Cs atom repels the molecule at this distance. This picture accounts qualitatively for the fact that there is little internal energy in the CsH product. The main energy release is in the form of a sudden strong impulse leading to a large relative kinetic energy and perhaps some rotational and vibrational excitation of the departing radical R.

Any molecule would be held tightly to the unreactive cesium ion oriented according to its polarizability tensor. The contraction of the $9p$ function accompanied by repulsion does not lead to reaction with most molecules but does leave the Cs atom in a lower electronic state, often the $6p$ state. The reactivity of Cs 9^2P with H_2 can perhaps be explained by the fact that the H atoms in the very small hydrogen molecule are held closer to the cesium ion than with the hydrocarbons. The lack of reactivity with the alkanes is explained by an impulsive repulsion between Cs and the molecule. The reactivity with propene is the hardest to explain. Its allylic C-H bond must help but a strong H-H bond did not prevent reaction. A possibility is that as the $9p$ wave function collapses it may localize on the carbon-carbon

double bond forming an ion pair which lasts long enough to permit reaction. Further experiments and theory are certainly needed to understand the reactions.

Inelastic collisions

The rate constant for collision induced decay of the Cs atom in the 9^2P state can be measured in two different ways, either by measuring the decay of fluorescence from the 9^2P or by measuring the rate of appearance of any of the final states, specifically the 6^2P states. The two values were 2.21×10^{-10} and $1.83 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. These two rate constants should be identical. The difference we ascribe to experimental error. It should be emphasized that we have not measured the individual rate constant for forming any particular final state but only a rate constant which is the sum of the rate constants to all possible final states. However, in the following an argument is presented that conversion to a 6^2P state is the most likely result of an inelastic collision.

The conversion of Cs 9^2P to 6^2P is a surprising result implying that the interaction of the Cs atom with the molecule has a largely scalar character which preserves the electronic angular momentum. It can be accounted for in the following way. Let \mathbf{r} and \mathbf{R} be vectors connecting the Cs nucleus with the electron and the center of mass of the molecule, respectively. Normally $|\mathbf{R}| \gg |\mathbf{r}|$, i.e., the molecule is external to the atom. In the present case the molecule is internal to the atom, i.e., closer to the Cs^+ ion core than is the electron. In this case $|\mathbf{r}| \gg |\mathbf{R}|$. The potential energy of interaction between the molecule and the electron depends on the distance $|\mathbf{r}-\mathbf{R}|$ which is approximately r . If we approximate the interaction as one between a point charge, the electron and a polarizable sphere, the energy of interaction is $-1/2\alpha E^2$ where E is the electric field of the electron at the center of mass of the molecule, $E = -e/|\mathbf{r}-\mathbf{R}|^2 \approx -e/r^2$. Therefore the interaction energy is $-1/2\alpha e^2/r^4$. The quan-

TABLE II. Bond energies and heats of reaction.^a

Reactant molecule, RH	R-H bond energy (kcal/mol)	ΔH^0 of reaction with Cs($9^2P_{3/2}$) (kcal/mol)
H_2	103.3	-17.6
CH_4	103.5	-17.4
C_2H_6	98.2	-22.7
$\text{CH}_3\text{CH}_2\text{CH}_3$	97.9 (CH_3), 95.2 (CH_2)	-25.7 (CH_2)
<i>c</i> - C_3H_6	106.3	-14.6
<i>c</i> - C_6H_{12}	95.5	-25.4
$\text{CH}_3\text{CH}=\text{CH}_2$	86.3	-34.6 (CH_3)

^aBond energies were taken from Ref. 9.

tities of interest are the matrix elements $\langle nl|1/r^4|n'l'\rangle$. Because the perturbation is independent of angle, angular momentum must be conserved, i.e., $l=l'=1$, for a p state, $n=9$ and $n'=8, 7$, or 6 . To sum up, the efficient n (but not l) changing collision is a consequence of the fact that during the collision the molecule is much closer to the Cs^+ ion than is the electron.

Because $1/r^4$ is so large near the Cs^+ ion, the $n=6$ state whose wave function is least diffuse will have the largest matrix element. A simple calculation was carried out for a hydrogenic atom with a nuclear charge $+Ze$. The squares of the matrix elements were

$$|\langle 91|r^{-4}|81\rangle|^2 = 4.21 \times 10^{-7} (Z/a_0)^8,$$

$$|\langle 91|r^{-4}|71\rangle|^2 = 6.26 \times 10^{-7} (Z/a_0)^8,$$

$$|\langle 91|r^{-4}|61\rangle|^2 = 9.88 \times 10^{-7} (Z/a_0)^8,$$

where a_0 is the Bohr radius.

The matrix element to the $6p$ state is further enhanced relative to those to the $8p$ and $7p$ states because the lower n wave functions are less screened from the large nuclear charge and therefore more concentrated. The overall matrix element is a product of the electronic matrix element briefly discussed here and a nuclear motion matrix element which, in principle, should vary with each molecule. In practice, similar yields of the 6^2P states were obtained in the collisions of all the alkanes.

SUMMARY

Cs atoms in the 9^2P state were shown to be unreactive with a number of alkanes including methane, ethane, pro-

pane, cyclopropane, and cyclohexane. These alkanes convert the atoms in the 9^2P states into lower $2P$ states. The excited atoms do react with propene, removing an allylic hydrogen atom to form CsH . This product is vibrationally cold and has only a modest amount of rotational energy, similar to the state distribution of the CsH product of the reaction with H_2 .

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