

Photochemistry in Van Der Waals Complexes: $(\text{Hg} - \text{H}_2)^* \rightarrow \text{HgH} + \text{H}$

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The $\text{Hg} - \text{H}_2$ collision complex in the reaction $\text{Hg}^{\text{3P}_1} + \text{H}_2$ has been investigated by a new method involving the Van der Waals complex of the reactants. This method yields the first observation of a vibrational transition in a reactive collision complex. Furthermore the fixed geometry of the Van der Waals complex corresponding to the Hg^{3P_1} state enables the separation of two different reaction paths depending on the electronic configuration of the complex, namely ${}^3\Sigma$ and ${}^3\Pi$.

INTRODUCTION

In a chemical reaction, the transition state is the key to the reaction in the Eyring Polanyi description.¹ To understand the reaction at the transition state many parameters must be known.

- the initial energy of the reactants (internal, translational);
- the geometry of the collision.

What is sought through an experimental probing of the transition state is:

- the potential curve transition state;
- the time evolution in the transition state;
- the energy flow into the fragments after selective excitation.

Even crossed beam experiments do not allow all parameters to be fixed, and they probe only indirectly the transition state through the analysis of the products.

We have devised a method which enables the direct observation of the reaction in the vicinity of the transition state in a photochemical

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reaction for a fixed geometry. The reactants are condensed in a Van der Waals complex in the ground state, then transferred by a tunable optical excitation into a selected state of the excited reactive surface. Then this surface can be analyzed through the characteristics of the observed spectrum (vibration, rotation, Franck-Condon factors).

This technique allows the study of the collision process in the fixed geometry of the excited state of the complex. As the collisional problem is replaced by a simpler photodissociation problem, the time evolution of the complex can be studied, the initial time being well-defined by the optical excitation.

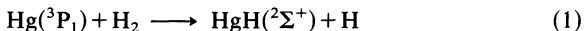
Experimentally simple (requiring only a supersonic free jet), the technique provides a high density of single collisions, necessary when the final products are spread over a large number of rovibronic states.

This technique has already been applied to the $(\text{Hg}-\text{Cl}_2)^3\text{P}_1 \rightarrow \text{HgCl}^* + \text{Cl}^2$ Van der Waals complex reaction, and has given conclusive evidence of a charge transfer intermediate in the reaction.

In the light of recent experiments on $\text{Mg} + \text{H}_2 \rightarrow \text{MgH} + \text{H}^3$ and on the $\text{Ca}(^1\text{P}_1) \rightarrow \text{HCl}$ system,⁴ where the reaction does depend on the geometric approach of the reactants, the Van der Waals method appears especially attractive, as the different approaches correspond to Van der Waals isomers or different electronic states of the complex.

The system we chose to investigate is $\text{Hg}(^3\text{P}_1) + \text{H}_2$, for the following reasons. Since it involves a light H_2 molecule, theoretical calculation should be possible. The small collisional quenching cross section of $\text{Hg}^3\text{P}_1 + \text{H}_2(30 \text{ \AA}^2)$ ⁵ suggests a rather slow process as compared to $\text{Hg}^3\text{P}_1 + \text{Cl}_2$ (*ca.* 100 \AA^2). Thus the complex spectrum should be structured.

It is known that, in the gas phase, the excitation of the resonant transition $\text{Hg}(6^1\text{S}_0 - 6^3\text{P}_1)$ in a mixture with H_2 leads to the formation of HgH ,⁶ through a direct mechanism:



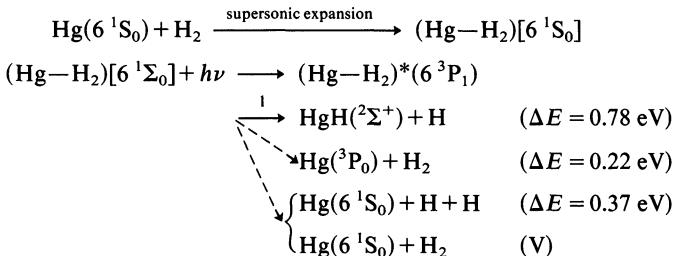
Nevertheless the importance of the competitive process



has not been clearly demonstrated.

The Van der Waals technique, involving a single half collision will allow the observation of the different paths of reaction and the branch-

ing ratio between channel 1 and 2. The experiment we propose is the following:



The final products Hg(3P_0) or HgH are then probed by laser induced fluorescence: the third channel is, however, a “dark channel”. In the experiments described hereafter we have observed as a dominant channel in the Van der Waals reaction (Hg 3P_1 , H₂) the HgH formation. Since the two electronic configurations Σ and Π of the complex exhibit a different behavior, we propose the system as an example of an orbitally selective reaction.

EXPERIMENTAL

The Hg–H₂ complex is prepared in a supersonic free jet, by the expansion of a mixture of He, Hg (0.1%), and H₂ (10%) at a pressure of 15 atm through a 200 μm nozzle. The complex is excited with a frequency doubled YAG pumped dye laser (50 μJ, 10 ns) and the products are probed by a nitrogen pumped dye laser (30 μJ, 5 ns) with a delay varying from 0 to 200 ns.

The Van der Waals complex reaction is characterized through:

(a) The fluorescence excitation spectra in the vicinity of the Hg($^3P_1 - ^1S_0$) transition. This reveals the nonreactive part of the potential surface, leading to fluorescence.

(b) The action spectra, where the complex excited states are populated with a tunable UV laser and a frequency fixed visible laser monitors the products formation through their laser induced fluorescence.

By this method

3P_0 is observed through excitation of the $6\ ^3P_0 - 7\ ^3S_1$ transition;

3P_1 is observed through excitation of the $6\ ^3P_1 - 7\ ^3S_1$ transition; $HgH(X^2\Sigma^+)$ is observed through excitation of the $HgH(^2\Sigma^+)v=0 - HgH(^2\Pi_{1/2}\sigma=0)Q_1$ branch.

RESULTS

To get an idea of what the excitation fluorescence spectrum of $Hg-H_2$ should be in the absence of reaction, i.e. a spectrum due purely to a Van der Waals optical transition, we have presented Figure 1a the $Hg-Ne$ Van der Waals complex fluorescence excitation spectrum. This complex has almost the same binding energy as the $Hg-H_2$ complex. As for $Hg-Ar$ and $Hg-N_2$,^{7,8} the $Hg-Ne$ spectrum contains two sets of lines blue and red shifted with respect to the $Hg\ ^3P_1 - \ ^1S_0$ transition. These sets of lines had already been assigned to vibrational progressions of two electronic states $^3\Sigma$ (blue shifted) and $^3\Pi$ in the collision induced absorption of mercury mixed with rare gases.⁹ In the case of sodium argon complexes, the rotational analysis identified the red shifted satellites of the sodium D lines unambiguously as the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ bands.¹⁰ The vibrational progression in the $^3\Sigma$ state converges to the dissociation limit, and the broad continuum following this vibrational progression corresponds, to the direct excitation above the dissociation limit of the $^3\Sigma$ state. In this region the complex should dissociate quickly, and then the observed fluorescence correspond to free $Hg\ ^3P_1$ atomic emission. This assumption has been verified through the direct observation of the $Hg\ ^3P_1$ atoms in the action spectrum displayed in Figure 1b. The same observation was done for the excitation of the structured continuum blue wing of the $Hg-N_2$ complex.⁷ Simultaneously, the appearance of the direct dissociation to $Hg\ ^3P_1$ in the $Hg-N_2$ complex is accompanied by the disappearance of the dissociation into the $Hg\ ^3P_0$ channel.

Figure 2a shows the fluorescence excitation spectrum of the $Hg-H_2$ complex. The only observed signal arises from the excitation of the $^3\Sigma$ state above the dissociation limit. As the H_2 should rotate freely, the states are labelled in $C_{\infty v}$ notation. The observed fluorescence is the $Hg\ ^3P_1$ free atom fluorescence, is verified through the 3P_1 action spectrum of the complex, coincident with the fluorescence excitation spectrum. Thus, contrary to the neon complex, we do not observe

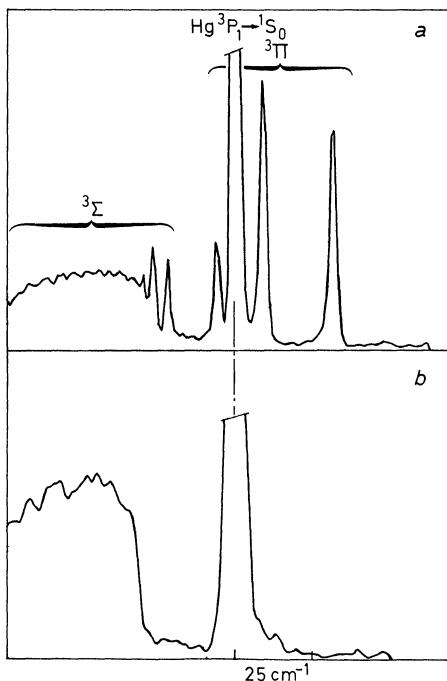


FIGURE 1a Fluorescence excitation spectrum of the Hg-Ne complex. $x/D = 30$, pure neon was used, $P_0 = 3$ atm. Partial pressure of Hg = 0.1 torr.

FIGURE 1b Action spectrum of the Hg-Ne complex. Excitation of the complex. Observation of the 3P_1 population through the excitation of the $6^3P_1 - 7^3S_1$ transition, and the observation of the resulting fluorescence $7^3S_1 - 6^3P_2$, $x/D = 30$. Pure neon was used, $P_0 = 3$ atm. Partial pressure of Hg = 0.1 torr. Delay between pump and probe laser 50 ns. The center line corresponds to the $6^3P_1 - 7^3S_1$ of the free uncomplexed mercury.

emission from the bound states of the excited complex with a signal to noise ratio of 10, a good indication that a nonradiative process (relaxation to 3P_0 , chemical reaction) occurs at a quicker rate (10^{+8} s^{-1}) than the fluorescence emission of the complex (10^{+7} s^{-1}). The chemical reaction within the complex is monitored through the action spectrum where the HgH laser induced fluorescence is observed (Figure 2b). The probe laser excites the $^2\Sigma V=0 - ^2\Pi_{1/2}, V=0$ transition, on the most intense $Q_1(3)Q_{12}(9)$ rotational transition, already observed in our preliminary gas phase collisional study which will be published later.

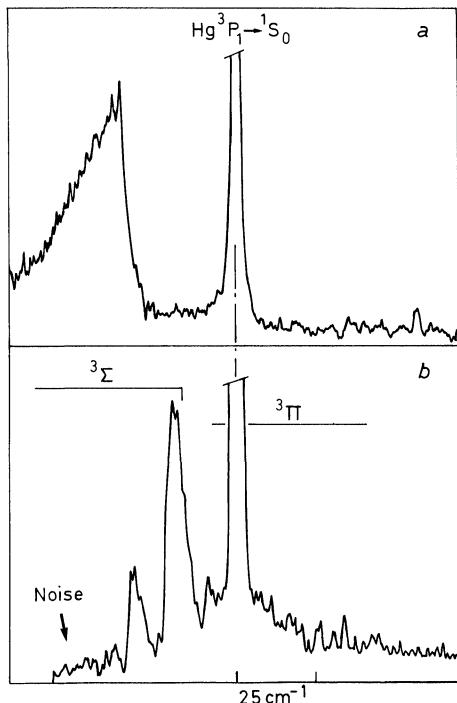


FIGURE 2a Fluorescence excitation spectrum of the Hg—H₂ complex. $x/D = 30$, mixture of He, H₂ (20% of H₂), $P_0 = 15$ atm. Partial pressure of mercury = 0.1 torr.

FIGURE 2b Action spectra of the Hg—H₂ complex. Excitation of the complex. Observation of the HgH molecule through the excitation of the $^2\Sigma^+ v=0$, $^2\Pi v=0$ (Q branch) transition, and the observation of the resulting fluorescence. $x/D = 30$, mixture of He, H₂ was used (20% of H₂), $P_0 = 15$ atm. Partial pressure of mercury = 1 torr. Delay between pump and probe laser 100 ns. The center line corresponds to the filter fluorescence induced by the emission of free mercury.

At the center of the action spectrum lies the Hg($^3P_1 - ^1S_0$) transition. Besides the mercury line, this spectrum exhibits two bands, the first one shifted to higher energy by $+22\text{ cm}^{-1}$, and the second weaker one by 35 cm^{-1} from the Hg($^3P_1 - ^1S_0$) transition. This second band ($+35\text{ cm}^{-1}$) lies just beyond the dissociation limit of the Hg—H₂ complex, above which no HgH laser induced fluorescence has been recorded. With our resolution (1 cm^{-1}) some rotational structure is observed within these bands. Starting from these two bands, going to

the red, a continuous signal has been observed down to 100 cm^{-1} . This signal does not show structure with our signal to noise ratio (≈ 3).

DISCUSSION

We have observed that not all the complex states yield HgH since the excitation of Hg—H₂ into the $^3\Sigma$ state above the dissociation limit yields the direct dissociation into Hg $^3P_1 + H_2$ instead of the reaction HgH. We thus have demonstrated that in the $^3\Sigma$ state a very small change in the energy of the system (10 cm^{-1} of a total of $40\,000\text{ cm}^{-1}$) drastically changes the reaction products.

The two blue shifted bands from the Hg($^3P_1 - ^1S_0$) transition can be, by comparison with other Hg Van der Waals complexes, assigned to vibrational levels of the $^3\Sigma$ state. The main band is then the vibrationless level and the second one can be assigned to one quantum of stretching.

The frequency of the dissociation limit observed in the fluorescence corresponds to the sum of the frequency of mercury transition and the ground state binding energy of the Hg—H₂ complex. Thus the 35 cm^{-1} of the blue shift of the dissociation limit from the 3P_1 line corresponds to $D_0(HgH_2, ^1S_0)$, bonding energy of the ground state. The bonding energy of the $^3\Sigma$ state is then 20 cm^{-1} ($35 - 22 + \frac{13}{2}\text{ cm}^{-1}$). The weakness of the bonding (20 cm^{-1}) is an argument which allows us to say that H₂ should rotate freely ($B_e = 60\text{ cm}^{-1}$).

As these vibrational bands are not broader than 10 cm^{-1} (including inhomogeneous broadening) the reaction leading to HgH is slow, not faster than 1 ps, but faster than 10 ns (absence of fluorescence signal from excited Hg—H₂).

As for the rare gas (and N₂) complexes of mercury, a vibrational progression in the $^3\Pi$ state as strong as for the $^3\Sigma$ state was expected. Instead, a weak continuum was found. It is then clear that the Π and Σ states do not exhibit the same behavior towards the chemical reaction. No conclusive interpretation can be given for this different behavior until potential surface calculations have been completed as well as vibrational and rotational energy distributions. The observed spectral broadening may originate from a very rapid reaction in the Π state and the weakness of the signal from a higher branching ratio to the Hg + H + H channel.

Nevertheless the difference in reactivity for the Π and Σ states can be understood in view of a correlation diagram of the molecular orbitals. This correlation diagram has been published for the similar reaction: $Mg(3P) + H_2$.¹¹ In the latter diagram it is shown that the Π state with a B_2 character in C_{2v} geometry can react while the Σ with A_1 character, cannot. This symmetry effect appears clearly in a pictorial view given in Figure 3, however not including the important spin orbit coupling of mercury.

CONCLUSION

These results are preliminary, but they already show the effect of the geometry (here the symmetry of the Van der Waals state) in a collision process. Among the future developments, the energy distribution in the fragment HgH versus the energy excitation in the complex, and the comparison with room temperature collision are in progress. Other extensions including the study of the $Hg\cdot D_2$ system, potential calculations, dynamic calculations and time resolved measurement are underway.

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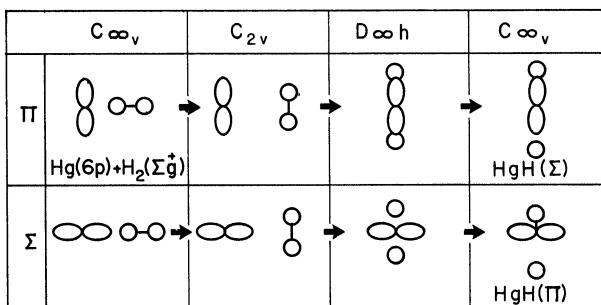


FIGURE 3 Pictorial correlation of the reagents orbitals.

References

1. H. Eyring and J. C. Polanyi, *Z. Phys. Chem. Abt. B* **12**, 279 (1931).
2. C. Jouvet and B. Soep, *Chem. Phys. Lett.* **96**, 426 (1983).
3. Wh. Breckenridge and H. Umemoto, *J. Chem. Phys.* **75**, 4153 (1981).
4. C. T. Rettner and R. N. Zare, *J. Chem. Phys.* **75**, 3636 (1981).
5. A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press).
6. A. C. Vikis and D. J. le Roy, *Can. J. Chem.* **51**, 1207 (1973); and ref. therein.
7. C. Jouvet and B. Soep, *J. Chem. Phys.* **80** (5), 2229 (1984).
8. S. Kato, R. L. Jaffe, A. Komonicki and K. Morokuma, *J. Chem. Phys.* **75**, 4567 (1983).
9. J. F. Kielkopf and R. A. Miller, *J. Chem. Phys.* **61**, 3304 (1974).
10. Behmen Burg, *Z. Naturforsch* **27a**, 31 (1972).
11. P. Chaquin, A. Sevin and H. Yu, to be published; N. Adams, W. H. Breckenridge and J. Simons, *Chem. Phys.* **56**, 327 (1981); R. P. Blikenderfer, K. D. Jordan, N. Adams and W. H. Breckenridge, *J. Chem. Phys.* **86**, 1930 (1982).