



HAL
open science

DIRECT OBSERVATION OF THE TRANSITION STATE OF A PHOTOCHEMICAL REACTION; THE Hg₃ P₁, Cl₂ SYSTEM

C. Jouvét, B. Soep

► **To cite this version:**

C. Jouvét, B. Soep. DIRECT OBSERVATION OF THE TRANSITION STATE OF A PHOTOCHEMICAL REACTION; THE Hg₃ P₁, Cl₂ SYSTEM. Journal de Physique Colloques, 1985, 46 (C1), pp.C1-313-C1-318. 10.1051/jphyscol:1985131 . jpa-00224508

HAL Id: jpa-00224508

<https://hal.science/jpa-00224508>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

DIRECT OBSERVATION OF THE TRANSITION STATE OF A PHOTOCHEMICAL
REACTION ; THE Hg 3P_1 , Cl $_2$ SYSTEM

C. Jouvét and B. Soep

*Laboratoire de Photophysique Moléculaire du CNRS, Bâtiment 213,
Université Paris-Sud, 91405 Orsay Cedex, France*

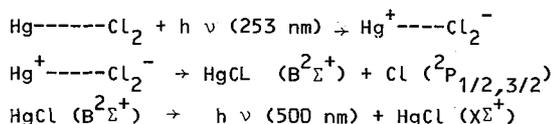
Résumé - Nous avons développé une méthode originale qui permet l'observation du complexe collisionnel dans une réaction photochimique, ce complexe conduisant à l'état de transition. Ici, les réactifs Hg, Cl $_2$ ont été condensés dans un complexe de van der Waals (Hg---Cl $_2$) puis portés par une excitation optique à 250 nm sur la surface réactive. Le spectre du complexe, extrêmement étendu, est attribuable à l'intermédiaire de réaction Hg $^+$ Cl $_2^-$.

Abstract - A novel method designed to observe the collision complex of a photochemical reaction is reported here. The reactants Hg, Cl $_2$ are frozen in a van der Waals complex (Hg---Cl $_2$), and then promoted by an optical excitation (250 nm) to the reactive state. The broad complex action spectrum, presumably due to the Hg $^+$ -Cl $_2^-$ intermediate, is monitored through the HgCl (B $^2\Sigma^+$) fluorescence.

The main difficulty in describing a chemical reaction lies in the discontinuity which arises at a given point between the reactants and the products. This discontinuity has been described as the transition state by Eyring and Polanyi (1). Since the early efforts (2) to observe directly such a state, key to the reaction, not many experiments have been conducted until recently (3). However such experiments are difficult as, during the short time of the reactive collision, the transition state is passed over rapidly with a considerable averaging over the impact parameter, and the internal states of the collision complex.

We describe herein a method leading directly to observation of the collision complex in photochemical reactions, the photochemistry of van der Waals complexes. Here the reactants are first frozen in the non reactive ground state of a van der Waals complex produced in a supersonic expansion, then a light pulse promotes this complex on the reactive potential surface. The immediate advantage of this method lies in its sensitivity: the number of observed species is directly proportional to the high number of van der Waals complexes suitably formed in the ground state. Moreover the optical excitation promotes selectively the cooled complex on a limited part of the reactive potential surface with fixed geometry and impact parameter, this surface being subsequently explored by the light pulse tuning, within the optical absorption limits.

Finally this method should allow a time dependent observation. We selected as a demonstrative example the Hg, Cl $_2$ system weakly reactive in the ground Hg(6^1S_0) state, owing to a $\approx 0,2$ eV barrier, and undergoing a chemiluminescent reaction in the (3P) Hg states. The reactions Hg + halogens have been extensively studied (4,9) and as proposed the Hg(3P_0,1,2) reaction mechanism involves Cl $_2$ harpooning through an electron jump, we suggest here the following reactions:



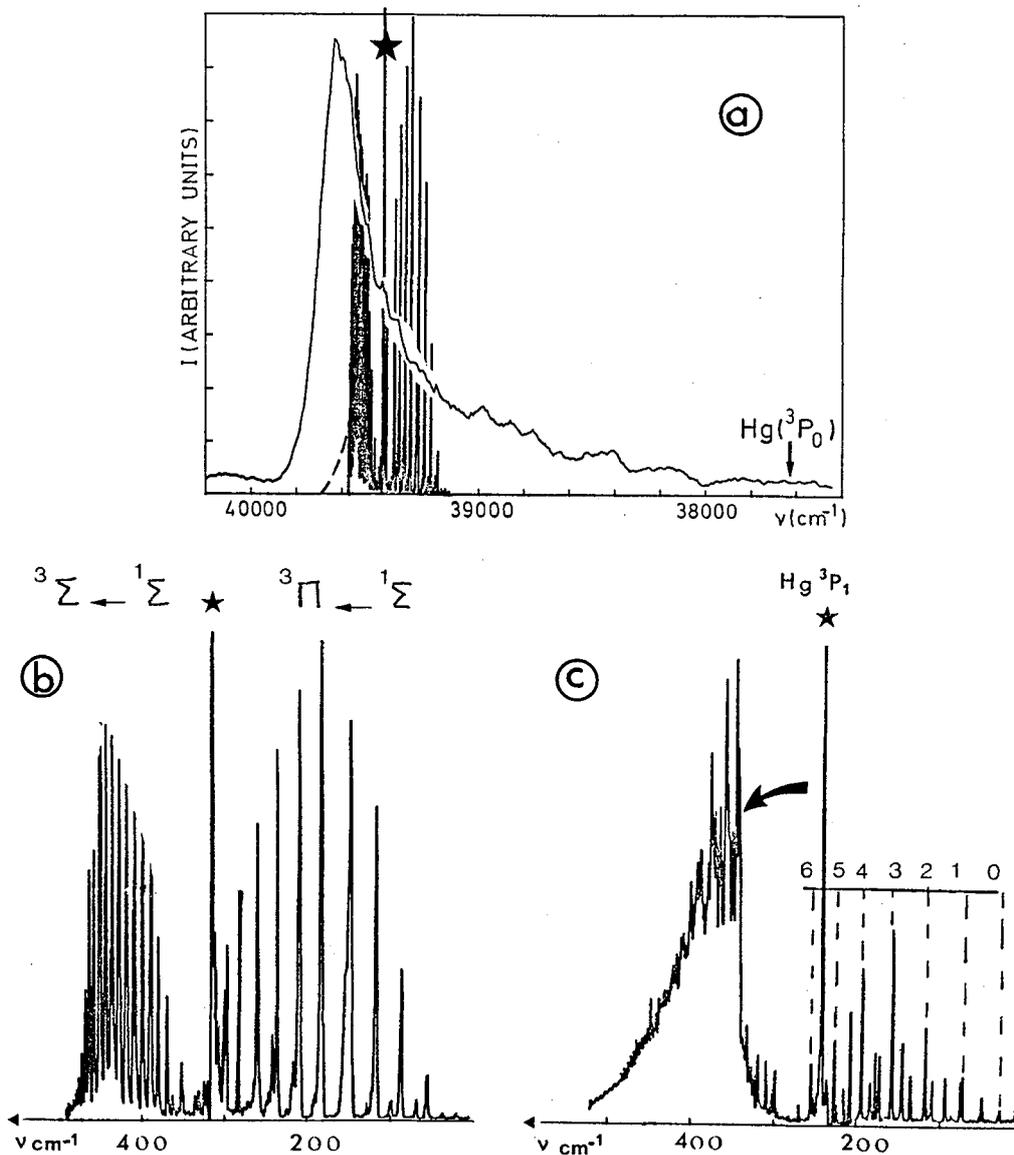


Figure 1 - a - Action spectrum of the Hg---Cl₂ complex in the 250 nm region with on the same scale the Hg-Kr fluorescence excitation spectrum
 b - Hg---Kr fluorescence excitation spectrum (enlarged)
 c - Hg---N₂ fluorescence excitation spectrum. The arrow indicates the onset of Hg ³P₁ + N₂ direct dissociation. The stretching vibration in the parallel state are labeled.

Thus the transition state $\text{Hg}^+ \cdots \text{Cl}_2^-$ will be directly evidenced through its fluorescence action spectrum, i.e the emission of $\text{HgCl } B^2\Sigma^+$.

EXPERIMENTAL

The supersonic jet apparatus is the same as previously described except for the pumping speed which has been increased to 2000 m³/h (5). We are working with a 200μm nozzle and a backing pressure of 20 bar. The chamber is maintained at a pressure less than 1 torr. The cooling efficiency was tested with benzene for which we measured a rotational temperature of 1°K.

As Hg and Cl₂ react at high temperature, we were obliged to build a double entry nozzle to minimize the interaction time between the two compounds at the temperature of 100°C used to vaporise the mercury. So the Hg seeded in He ($\approx 5 \times 10^{-5}$ Hg/He) is mixed with Cl₂ diluted in He (10^{-2} Cl₂/He) at 1 mm upstream the nozzle. When Cl₂ was added its molar fraction was less than 0,5 %.

We verified the effectiveness of this small transit time system, monitoring the mercury signal in presence of chlorine but in a pressure domain outside van der Waals complexes formation ($P_0 < 2$ bar). The jet is crossed at 5 to 7 nm downstream by the beam of a YAG (Quantel) pumped dye laser (home made), frequency doubled by means of an angle tuned lithium formate crystal. The fluorescence light is collected on a photomultiplier (RCA 8850) through filters which allow only the $\lambda > 500$ nm light to be detected, or it is dispersed by a .75 m Jobin Yvon monochromator.

RESULTS AND DISCUSSION

We have observed in the 250 nm (40 000 cm⁻¹) spectral region a fluorescence action spectrum displayed in fig. 1a that we ascribe to the Hg---Cl₂ complex.

- 1) The action spectrum is characteristic of the cooled jet zone : the fluorescence signal disappears when the exciting light pulse probes a "hot" domain.
- 2) This spectrum is due to a mixed Hg, Cl₂ van der Waals complex, its intensity increasing rapidly with the backing pressure P₀, the relative or absolute concentrations of mercury and chlorine. However some stable HgCl₂ is formed in the ground state before the expansion. But the UV fluorescence emission of HgCl₂ excited around 250 nm is very weak and it cannot energetically yield fluorescent HgCl (fig. 2).

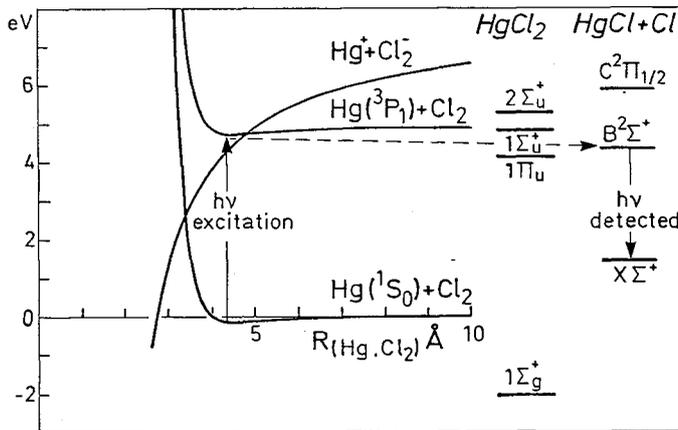


Fig. 2 - Partial potential energy diagram with entrance and exit channels indicated

3) When exciting the complex at the maximum of the absorption spectrum, the resulting dispersed emission can be clearly identified in Fig. 3 as the HgCl $B^2\Sigma^+ \rightarrow X^2\Sigma^+$.

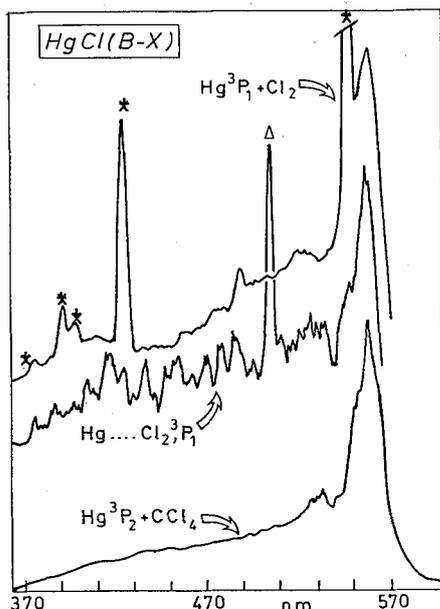


Fig. 3.- Emission spectra of HgCl (B-X). From top to bottom : - emission spectrum of $Hg^3P_1 + Cl_2$ reacting in thermal collision conditions. Asterisks denote mercury emission lines. - emission spectrum resulting from the excitation of the complex at the maximum (39600 cm^{-1}) of the $Hg\text{---}Cl_2, ^3P_1$ action spectrum. - emission spectrum reproduced from Setser et al ref (8) resulting from the collisions of $Hg^3P_2 + CCl_4$ thermal collision. Δ indicates laser scattered light.

The action spectrum 1a is very broad (1000 cm^{-1}) and diffuse even with a $0,1\text{ cm}^{-1}$ laser resolution and a signal to noise ratio of 20. The spectral excitation domain overlaps the Hg transitions ($^1S_0 \rightarrow ^3P_1$) and ($^1S_0 \rightarrow ^3P_0$, forbidden), stopping abruptly + 200 cm^{-1} above the resonance line.

We can show, comparing with the fluorescence excitation spectra of other mercury van der Waals complexes, that the action spectrum is intrinsically diffuse and does not correspond to an upper van der Waals state. The krypton mercury van der Waals complex excitation spectrum is shown in fig. 1b together with the nitrogen complex (fig. 1c). The spectra appear as almost line like and exhibit two distinct lobes corresponding, in the krypton-Hg spectrum to the $^3\Pi + ^1\Sigma$ (red-shifted) $^3\Sigma + ^1\Sigma$ (blue shifted) transitions. In both cases the spectrum is restricted to a few hundred wavenumbers as compared to $Hg\text{---}Cl_2$ which extends over 2000 cm^{-1} . From the vibrational analysis (7) of the HgN_2 , $HgKr$ spectra the binding energy of the complexes ranges between 100 cm^{-1} and 300 cm^{-1} in the excited states. Thus the increased polarizability of chlorine (twice krypton's) cannot account for the extension of the $HgCl_2$ spectrum and the upperstate bonding energy of the complex.

Moreover the observed diffuseness cannot be ascribed to sequence congestion owing to the low temperatures achieved in the supersonic expansion. The HgN_2 spectrum is of course more complex than the diatomic spectrum of $HgKr$, but clear progressions can be identified leading at the blue edge to a quasi-continuum. This continuum in

the HgN_2 spectrum corresponds to the direct excitation of the repulsive curve of the vdy excited potential leading to $\text{Hg } ^3\text{P}_1 + \text{N}_2$. We verified (7) this, monitoring the $\text{Hg } ^3\text{P}_1$ atoms with a probe laser on the $\text{Hg } 7^1\text{S}_1 \leftarrow 6^3\text{P}_1$ transition. We repeated the experiment over the entire Hg--Cl_2 action spectrum, probing the $^3\text{P}_1$ Hg atoms without detecting any $^3\text{P}_1$ signal. Thus the continuous character of the HgCl_2 action spectrum does not originate from unresolved vibrational structure nor from dissociation to $\text{Cl}_2 + \text{Hg } ^3\text{P}_1$. We must consider that the action spectrum is intrinsically diffuse due to the rapid reaction $\text{Hg--Cl}_2, (^3\text{P}_1) \rightarrow \text{HgCl (B)} + \text{Cl}$.

Such a deep Hg--Cl_2^* upper state must correspond to a mixed state resulting from the strong interaction of the locally excited van der Waals with the neighbouring states. The most likely candidate is the Hg^+, Cl^- charge transfer state as it crosses the vdw curve at a distance near the ground state equilibrium geometry. The presence of the charge transfer state has also been accounted for in the laser assisted reaction $\text{Xe} + \text{Cl}_2$ (10).

The very rapid reaction indicates that one scans optically a downward valley, the transition state being entirely repulsive as in the electron jump mechanism.

We then probed the internal energy distribution of the products $\text{HgCl B } ^2\Sigma^+$ issued from the reaction whose emission spectrum is very sensitive to internal state population (8). We observed that the emission spectrum HgCl B-X obtained from excitation at the maximum of the complex action spectrum (fig. 3 middle trace) is similar to the one obtained by the thermal reaction $\text{Hg } ^3\text{P}_1 + \text{Cl}_2$ (fig. 3 top). Furthermore these emission spectra are closely matched by the spectrum obtained with the reaction $\text{Hg } ^3\text{P}_2 + \text{CCL}_4$ (fig. 3 bottom) whose excess energy is identical (0,8 eV). Thus, the similar energy distribution in the HgCl fragment for the complex reaction and the thermal $\text{Hg } ^3\text{P}_1 + \text{Cl}_2$ and Hg^+CCL_4 indicates that the reaction pathways depend more on the excess energy in the reactants than on the reaction geometry. The HgCl B-X emission spectrum should then be an interesting probe of the reactive surface utterly sensitive to excess energy, in the $(\text{Hg--Cl}_2)^*$ complex.

In conclusion this van der Waals complex reaction has enabled the direct probe of the $\text{Hg--Cl}_2, (^3\text{P}_1)$ reaction surface revealing the Hg^+, Cl^- intermediate. We are currently investigating other systems such as $\text{Hg--H}_2, (^3\text{P}_1)$ where we expect to observe a structured intermediate spectrum owing to the much smaller reaction cross section (8 \AA^2) of the $\text{Hg } ^3\text{P}_1 + \text{H}_2 \rightarrow \text{HgH}$ reaction. Detailed spectroscopic information should lead to a precise and direct knowledge of the reactive potential surface.

REFERENCES

- 1 - EYRING M. and POLANYI M., J. Phys. Chem. Abt B, 12 (1951) 279
- 2 - POLANYI M., Z. Phys. 3 (1920) 31
- 3 - FOTH M.J., H.H. TELLE and POLANYI J.C., J. Phys. Chem. 86 (1982) 5027
WILCOMB B.E. and BURNHAM, J. Chem. Phys. 74 (1981) 6784
MAGUIRE T.C., BROUKS P.R. and CURL Jr R.F., Phys. Rev. Lett. 50 (1983) 1918 and accompanying paper
- 4 - ROXLO C.B., Master Thesis MIT (1979)
DREILING T.D., Ph. D. Thesis Kansas University (1982) and references therein
MAYER T.M., MUCKERMAN J.T., WILCOMB B.E., BERNSTEIN R.B., J. Chem. Phys. 67, (1977) 3522
KRAUSE H.F., JOHNSON S.G., DATZ S. and SCHMIDT-BLEEK F.K., Chem. Phys. Lett. 31 (1975) 577
- 5 - SOEP B., TRAMER A., Chem. Phys. Lett. 64 (1979) 485
JOUVET C., Thèse Orsay 1981
- 6 - TANG K.Y., HUNTER R.O., OLDENETTEL Jr and J., HUESTIS D.L., J. Chem. Phys. 70 (1979) 1492

- 7 - JOUVET C. and SOEP B., to be published
- 8 - DREILING T.D. and SETSER D.W., J. Chem. Phys. 79 (1983) 5423
- 9 - WEINER J., J. Chem. Phys. 72 (1980) 5731
- 10 - KU J.K., INOUE G. and SETSER D.W., J. Chem. Phys. 87 (1983) 2989