行政院國家科學委員會專題研究計畫 成果報告

在 Para -氫間質的分子過程的研究
研究成果報告(精簡版)

計 畫 類 別 ：個別型
計 畫 編 號 ：NSC 99-2113-M-009-015-
執 行 期 間 ：99 年 08 月 01 日至 100 年 07 月 31 日
執 行 單 位 ：國立交通大學應用化學系（所）

計 畫 主 持 人：寺西慶哲

計畫參與人員：碩士班研究生-兼任助理人員：彭冠偉

公 開 資 訊 ：本計畫可公開查詢

中 華 民 國 100 年 11 月 15 日

中 文 摘 要 ： 作為間質材料 para-氫(pH2)已經引起許多人的注意，有以下幾個理由。首先，氫氣是最輕的分子，從而導致大的零點能和隧道效應。這就是為什麼固體氫會被稱為量子固體。其次，pH2 在低溫條件下 J=0，具有球形對稱。這導致了小的分子間相互作用力，晶格常數大以及籠效應小。Momose 等測量 CD4 分子在 pH2 間質中的振動轉動光譜，發現 P(1)峰過渡 v4 的模式有一個寬 0.012cm-1，其中作為光譜 v3 的模式有更廣泛的寬度。

據透露，一些光譜會和 pH2 間質具有很大的雜質效應。舉例來說，少量的稀有氣體雜質會經由 pH2 禁止氣相中的誘導紅外線的吸收。ortho-氫(oH2)的不純也起了重要的作用，這是因為 oH2 是自然存在的雜質，具有非零角動量 J=1，從而導致四極矩。由於四極矩弱的長範圍相互作用，oH2 能夠聚在一起，形成 oH2 集群與摻雜客體分子。

雖然 pH2 的量子性質提供了客體分子的有趣光譜，然而詳細的理論工作還尚未完成，在大多數的情況下其實結果是與氣相譜做分配比較。我計劃發展一個從頭算理論來解決 pH2 在超低溫條件下的光譜和動力學問題。我會從一個 pH2 二聚體及客體分子的量子化學計算開始。它也可能討論 oH2 雜質效應取代客體分子的 OH2。在詳細分析這些種二聚體，我會使用雙重絕熱近似法去考慮系統的問題即客體分子被嵌入在一個固體 pH2。由於在實驗中的分子動力學利用間質隔離光譜法，pH2 分子光譜具有極為重要的研究動態以及淵博知識。我將使用一個定量的理論去回答為什麼有些光譜是狹窄的高峰而有些卻不是。

中文關鍵詞： 量子化學, 光譜形狀, 隧道, 間質隔離, 量子固體

英 文 摘 要 ： Para-hydrogen has attracted much attention as a matrix material. There are several reasons for this. First, hydrogen is the lightest molecule, which leads to large zero point energy and tunneling effect. This is why solid hydrogen is called quantum solid. Second, pH2 is in J=0 state in a low temperature limit having spherical symmetry. This leads to small intermolecular interactions, large lattice constant, and small cage effects. Momose et al. measured rovibrational spectra of CD4 molecule in pH2 matrix, and found that the peak of P(1) transition of v4 mode has a width of 0.015 cm-1, where as the spectra of v3 mode has broader width.

It is revealed that some spectra with pH2 matrix have large impurity effects. For example, small amount of rare gas impurity induces IR absorption by pH2 that is forbidden in the gas phas. ortho-hydrogen (oH2) impurity also plays significant roles. This is because oH2 is naturally existing impurity having non-zero angular momentum J=1, leading to quadrupole moment. Due to the weak long range interaction with the quadrupole moment, oH2 can get together forming an oH2 cluster with the doped guest molecule.

Even though quantum nature of pH2 provides interesring spectra of the trapped molecules, detailed theoretical work has not been done, and experimental results are assigned by the comparison with the gas phase spectra in most of the cases. I am planning to develop an ab initio theory to solve spectroscopic and dynamical problems with pH2 in ultra cold conditions. I am going to start from a quantum chemical calculation of a dimer that consists of a pH2 and the guest molecule. It is also possible to discuss the oH2 impurity effect by replacing the guest molecule by oH2. After the detailed analysis of these kinds of dimers, I will consider the system in which the guest molecule is embedded in a solid pH2 by using dual adiabatic approximation. Since the experiments on dynamics of molecules in matrix utilize spectroscopic method, profound knowledge of molecular spectra in pH2 has a crucial importance in studies of dynamics as well. I would like to answer using a quantitative theory why some spectra show extremely narrow peaks whereas others are not.

英文關鍵詞： Quantum Chemistry, Spectral Shape, Tunneling, Matrix Isolation, Quantum Solid

附件一

行政院國家科學委員會補助專題研究計畫 ■ 成 果 報 告 □期中進度報告

在 Para-氫間質的分子過程的研究

(Molecular Processes in Para-Hydrogen Matrix)

計畫類別：■個別型計畫　□整合型計畫
計畫編號：NSC 99－2113－M－009－015－
執行期間： 2010 年 08 月 01 日 至 2011 年 07 月 31 日

執行機構及系所：交通大學/應化系

計畫主持人：寺西 慶哲 (Yoshiaki Teranishi)
共同主持人：
計畫參與人員：彭冠偉

成果報告類型(依經費核定清單規定繳交)：■精簡報告　□完整報告

本計畫除繳交成果報告外，另須繳交以下出國心得報告：
□赴國外出差或研習心得報告
□赴大陸地區出差或研習心得報告
□出席國際學術會議心得報告
□國際合作研究計畫國外研究報告

處理方式：除列管計畫及下列情形者外，得立即公開查詢
□涉及專利或其他智慧財產權，□一年□二年後可公開查詢

中　華　民　國　2011　年　10　月　31　日

附件二

國科會補助專題研究計畫成果報告自評表

請就研究內容與原計畫相符程度、達成預期目標情況、研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性）、是否適合在學術期刊發表或申請專利、主要發現或其他有關價值等，作一綜合評估。

1. 請就研究內容與原計畫相符程度、達成預期目標情況作一綜合評估

■ 達成目標

□ 未達成目標（請說明，以 100 字為限）

□ 實驗失敗

□ 因故實驗中斷

□ 其他原因

說明：

We have discussed (1) Tunneling of impurity molecule (ortho-H_2 and HD molecule) in solid para-H_2 matrix, and (2) Mode dependence of the vibrational spectra of methane in para-H_2 matrix.

(1) Shevtsov et al (Phys. Rev. **B62**, 12386, (1995)). performed quantum diffusion constant of ortho-H_2 in para-H_2 matrix. They obtained so called the Arrhenius plot (plot the rate constant versus the inverse of temperature). M. Rall et al (Phys. Rev. **B45**, 2800 (1990)). has performed a series of experiment of nuclear spin-spin relaxation of HD impurity in para-H_2 matrix. This relaxation is attributed to tunneling diffusion of HD molecule. An interesting point in their experiment is that the spin relaxation time has positive and negative slope as function of the temperature. We found that those two experimental results can be explained by a simple theory utilizing the second order purtabation theory, in which the thermal rate constant W is given by $W=\sum_k P_k W_k$. Here P_k and W_k are respectively the Bolzmann distribution constant and single level rate constant given by

$$W_k=\sum_m \Omega_m=\frac{2\pi}{\hbar^2}\sum_m\left|H'_{mk}+\sum_n\frac{H'_{mn}H'_{nk}}{\hbar\omega_{kn}}\right|^2\delta(\omega_{mk})$$

A simple form of Ω_m is obtained assuming tunneling take places between shifted harmonic potentials with large shift, which leads to

$$\Omega_m\propto\sqrt{\frac{2\pi}{S\omega^2(2\bar{n}+1)}}\exp\left[-\frac{(\Delta E+S\omega)^2}{2S\omega^2(2\bar{n}+1)}\right]$$

where S and ω are the Huang-Rhys factor and the harmonic frequency, respectively. This simple theory can explain both the experimental results nicely (see fig.1).

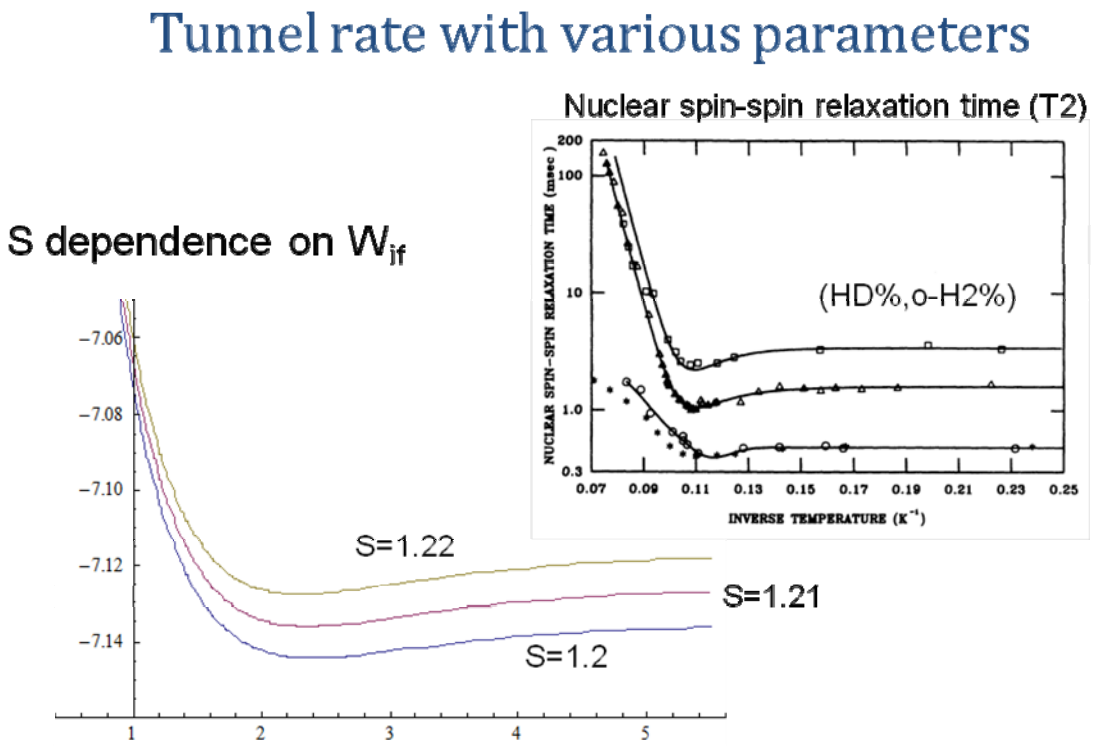

Fig.1 Our theoretical result (left) and the experimental result by Rall et al.

(2) Momose et al. discussed experimentally the rovibrational spectra of CD_4 molecule in para-H_2 matrix. Their results shows that the v4 mode has very narrow line width, and nearly zero width at zero temperature limit. v3 mode, on the other hand, has relatively broad peak, which is nonzero at low temperature limit (see Fig.2).

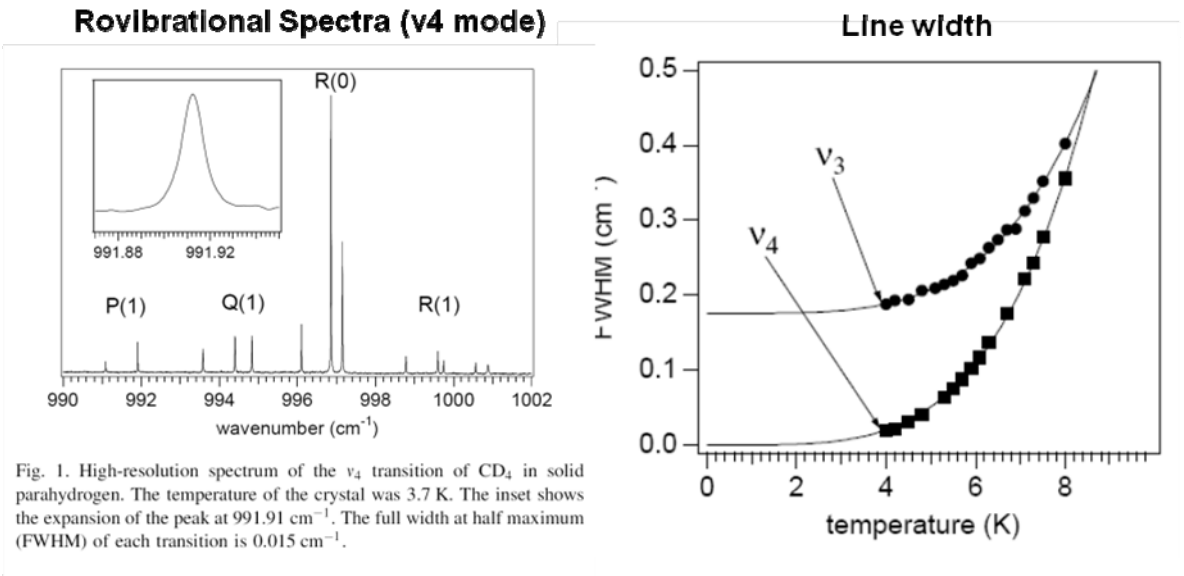

Fig.2 Experimental result by Momose et al.

We have performed quantum chemical calculations of the CD_4-paraH_2 interaction as function of intermolecular distance. Here we assume dual adiabatic approximation, in which both the electronic and inner molecular rovibrational degrees of freedom are regarded as “fast” variables, whereas the inter molecular distance is treated as the adiabatic parameter. As for the v4 mode the CD_4-paraH_2 interaction is shown in Fig.3. Here the red (green) line is for the ground (v4 excited) rovibrational adiabatic states.

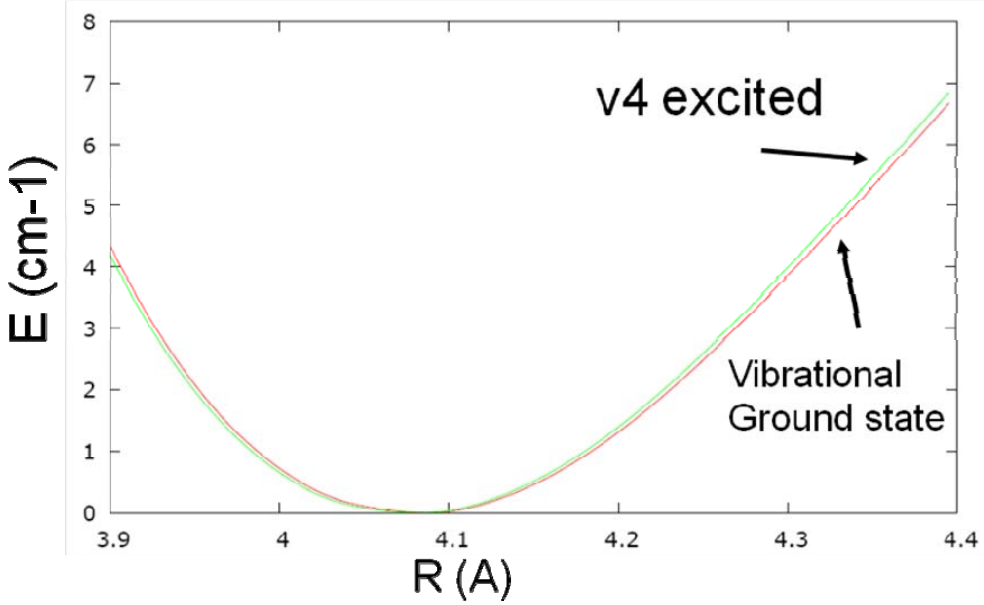

Fig.3 Dual adiabatic potentials (ground and v4 excited)

As is seen from Fig.3, v4 excited potential is not shifted from the ground one. This leads to the zero width at the low temperature limit. On the other hand, As is shown in Fig.4, adiabatic potential of v3 excited state is shifted from the ground state potential, which leads to nonzero width at the zero temperature limit.

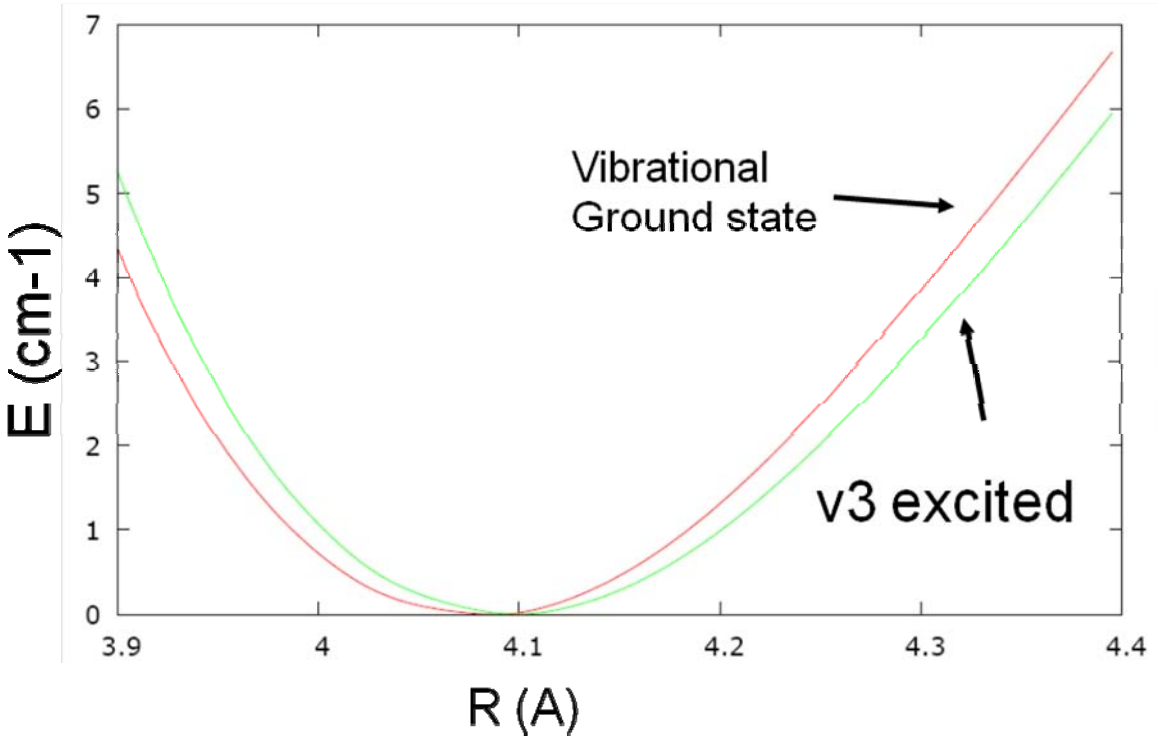

Fig.4 Dual adiabatic potentials (ground and v3 excited)

So far we have discussed only the dual adiabatic potentials. It is, however, possible to calculate the spectral positions and shapes if we include the H_2-H_2 interactions. This is what we are currently working on.

2. 研究成果在學術期刊發表或申請專利等情形：

論文：□已發表 □未發表之文稿 ■撰寫中 □無

專利：□已獲得 □申請中 □無

技轉：□已技轉 □洽談中 □無

其他：(以 100 字為限)

3. 請依學術成就、技術創新、社會影響等方面，評估研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性）(以 500 字為限)

Our theory of thermal rate constant shows that various different processes can be understood in a unified way. Our theory can basically discuss general rate processes in the low temperature limit, and we have shown that these processes are characterized by several parameters, the Huang-Rhys factors and harmonic frequencies. Our theory is not quantitatively accurate, since anharmonic effects are not negligible in H_2-H_2 interaction. It is possible to have a better representation of Ω_m, which enables us to discuss the low temperature thermal rate processes quantitatively. The important consequent in the present simple theory is in providing a unified way of understandings.

Narrow linewidth of molecule in para-H_2 is a very important property of solid H_2 matrix technique. This is basically attributed to the small intermolecular interactions (small cage effect) of solid H_2. Actual mechanism, however, is not simple. As Momose et al. has shown, linewidth has mode dependence and temperature dependence. This kind of complicated mechanism is discussed by the dual adiabatic approximation. As is shown in Fig.3 and Fig.4, simple adiabatic potentials tells the information on mode dependence of the linewidth. This new theory provides a new viewpoint on the spectra of molecule in solid H_2 matrix.

These new aspects of our studies can be applied various spectra and dynamical processes in solid H_2 matrix. We expect that our theory can contribute to the para-H_2 matrix science society.

國科會補助計畫衍生研發成果推廣資料表

日期:2011/11/05

國科會補助計畫	計畫名稱: 在Para -氫間質的分子過程的研究
	計畫主持人: 寺西慶哲
	計畫編號: 99-2113-M-009-015- 學門領域: 物理化學

無研發成果推廣資料

99 年度專題研究計畫研究成果彙整表

計畫主持人：寺西慶哲	計畫編號：99-2113-M-009-015-
計畫名稱：在 Para -氫間質的分子過程的研究	

成果項目			量化			單位	備註（質化說明：如數個計畫共同成果、成果列為該期刊之封面故事...等）
			實際已達成數（被接受或已發表）	預期總達成數(含實際已達成數)	本計畫實際貢獻百分比		
國內	論文著作	期刊論文	0	1	100%	篇	撰寫中
		研究報告/技術報告	0	0	100%		
		研討會論文	0	0	100%		
		專書	0	0	100%		
	專利	申請中件數	0	0	100%	件	
		已獲得件數	0	0	100%		
	技術移轉	件數	0	0	100%	件	
		權利金	0	0	100%	千元	
	參與計畫人力（本國籍）	碩士生	1	1	100%	人次	計畫相關資料收集、匯整及其它交辦事項。
		博士生	0	0	100%		
		博士後研究員	0	0	100%		
		專任助理	0	0	100%		
國外	論文著作	期刊論文	0	0	100%	篇	
		研究報告/技術報告	0	0	100%		
		研討會論文	0	0	100%		
		專書	0	0	100%	章/本	
	專利	申請中件數	0	0	100%	件	
		已獲得件數	0	0	100%		
	技術移轉	件數	0	0	100%	件	
		權利金	0	0	100%	千元	
	參與計畫人力（外國籍）	碩士生	0	0	100%	人次	
		博士生	0	0	100%		
		博士後研究員	0	0	100%		
		專任助理	0	0	100%		

其他成果 (無法以量化表達之成果如辦理學術活動、獲得獎項、重要國際合作、研究成果國際影響力及其他協助產業技術發展之具體效益事項等，請以文字敘述填列。)	無。

	成果項目	量化	名稱或內容性質簡述
科教處計畫加填項目	測驗工具(含質性與量性)	0	
	課程/模組	0	
	電腦及網路系統或工具	0	
	教材	0	
	舉辦之活動/競賽	0	
	研討會/工作坊	0	
	電子報、網站	0	
	計畫成果推廣之參與（閱聽）人數	0	

國科會補助專題研究計畫成果報告自評表

請就研究內容與原計畫相符程度、達成預期目標情況、研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性）、是否適合在學術期刊發表或申請專利、主要發現或其他有關價值等，作一綜合評估。

1. 請就研究內容與原計畫相符程度、達成預期目標情況作一綜合評估

■達成目標

□未達成目標（請說明，以 100 字為限）

□實驗失敗

□因故實驗中斷

□其他原因

說明：

2. 研究成果在學術期刊發表或申請專利等情形：

論文：□已發表 □未發表之文稿 ■撰寫中 □無

專利：□已獲得 □申請中 ■無

技轉：□已技轉 □洽談中 ■無

其他：(以 100 字為限)

3. 請依學術成就、技術創新、社會影響等方面，評估研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性）(以 500 字為限)

These new aspects of our studies can be applied various spectra and dynamical processes in solid H2 matrix. We expect that our theory can contribute to the para-H2 matrix science society.