

行政院國家科學委員會專題研究計畫 期中進度報告

大氣化學中重要分子的光物理及光化學(1/3)

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中文摘要

此國際合作計劃係植基於比利時布魯塞爾自由大學光化學物理中心與交通大學應用化學系/分子科學研究所雷射實驗室在光譜學上之優越傳統以及兩個實驗室的既存之友誼及合作關係，計劃中研究大氣化學中重要分子在氣態及低溫間質隔離態的光物理及光化學。吾人利用兩個實驗室中極為相輔相成的儀器設備及專門技術來研究這些分子。第一年計劃已順利開展，有關 SO \tilde{B} 高度預解離電子態的研究，吾人擴展合作對象而包括英國的 Colin Western 教授，利用其 PGOPHER 程式來研究微擾，初步結果已在 2005 年 9 月於瑞士舉行的第 28 屆國際自由基研討會發表。有關高泛頻光譜之研究，吾人已利用腔內衰減完成 CO(5-0) 之測量工作，並已發表於 J. Phys. Chem.，此係世界上的首次測量，且發現了 P 與 R 譜帶的強度反轉。有關內轉動之研究，吾人也已完成 CH₃OH 在 p-H₂ 的研究，首次証實 CH₃OH 在固態 p-H₂ 中仍有內轉動，且此方法可以協助氣態的光譜指認，也可以研究核自旋的弛緩。此論文已送往 Science 投稿。主持人於 8 月 30 日至 9 月 4 日赴比利時布魯塞爾與 Colin 及 Herman 教授討論，並發表演講，Herman 教授亦於 3 月 21 日至 28 日來台參訪討論。同時，目前安排博士班學生於 2006 年初赴布魯塞爾參與研究。

關鍵字：間質隔離、腔內衰減、CO、SO、CH₃OH、p-H₂

英文摘要

This project builds on an existing collaboration and on the historical strength of the two laboratories, Service de Chimie quantique et Photophysique, Université libre de Bruxelles (ULB) and the Laser Chemistry Laboratory, Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University (NCTU) to investigate the photophysics and chemistry of molecular species of importance to atmospheric chemistry, either in the gas phase or in low-temperature matrices.

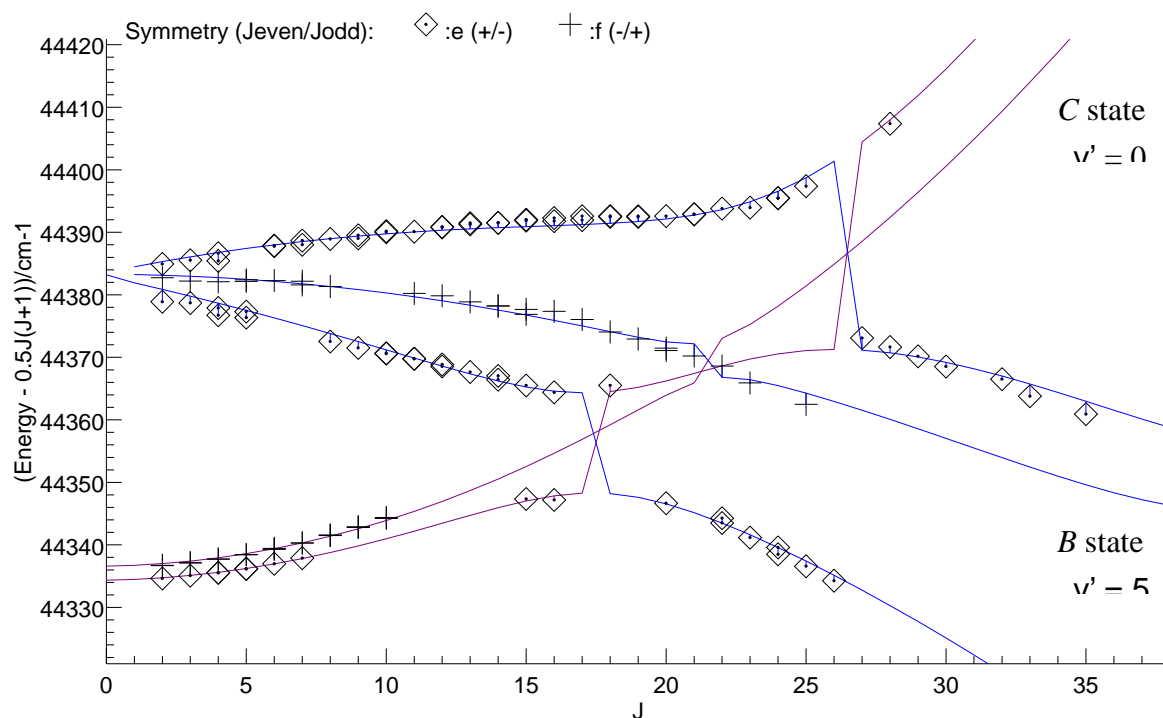
Research for the first year is going well. We have expanded the collaboration on the highly predissociative levels of the \tilde{B} state of SO to include Prof. Colin Western at Univ. Birstol, UK who wrote a PROPHER program to handle the perturbation. Preliminary results are presented in the 28th International Symposium on Free Radicals, held in Switzerland in September, 2005. We also measured absorption of CO (5-0) band with cavity ringdown technique. The work has been published in J. Phys. Chem.; it is the first measurements and

the intensity inversion for the P/R bands was reported. We have also recorded IR spectra of CH₃OH isolated in solid p-H₂ and identified for the first time the presence of internal rotation in such an environment. This is a new technique to help spectral assignments in the gas phase; it can also be used for studying nuclear spin conversion. The work has been submitted for publication in Science. The PI visited Brussels from August 30 to September 4, 2005 and discussed with Professors Colin and Herman. Professor Herman also visited Taiwan from March 21 to March 28, 2005. Now we are arranging a Ph.D. student to visit Brussels for 2-3 months to participate experimental work.

Keywords: matrix isolation, cavity ringdown, CO, SO, CH₃OH, p-H₂

1. **"Deperturbation of electronic states of SO above the first dissociation limit"**, R. Colin, N. L. Elliott, Y.-P. Lee, C.-P. Liu, and C. M. Western, 28th International Symposium on Free Radicals, Leysin, Switzerland, Sept. 4-9, 2005.

The $B^3\Sigma^- - X^3\Sigma^-$ transition of SO has been the subject of many studies over the past years. Its spectral complexity is due to interactions with a number of overlapping electronic states, such as the $C^3\Pi$ and $d^1\Pi$ states. This poster discusses the perturbations affecting a number of vibrational levels within the $B^3\Sigma^-$ state. The analysis is based on SO spectra obtained in several laboratories by a variety of methods, and used the PGOPHER program [1]. The energy level plot below results from an initial attempt at deperturbing the $v' = 5$ level of the $B^3\Sigma^-$ state, which is crossed by the $\Omega = 0$ component of the $C^3\Pi$ state ($v' = 0$).



[1] PGOPHER program, C. M. Western, <http://pgopher.chm.bris.ac.uk>

2. **"Detection of Vibration-Rotational Band 5 – 0 of $^{12}\text{C}^{16}\text{O X }^1\Sigma^+$ with Cavity Ringdown Absorption Near 0.96 μm "**, C.-Y. Chung, J. F. Ogilvie, and Y.-P. Lee, J. Phys. Chem. 109, 7854 (2005).

We have recorded extremely weak absorption in overtone band 5 – 0 of $^{12}\text{C}^{16}\text{O X }^1\Sigma^+$ near 0.96 μm with cavity ringdown spectroscopy; the light source was a Raman-shifted dye laser pumped with a frequency-doubled Nd:YAG laser. This band shows lines in branch P to be much more intense than corresponding lines in branch R, in contrast to all

lower overtone bands $\nu - 0$ ($\nu = 1 - 4$). This reversal in relative intensity is explained quantitatively in terms of a radial function for the electric dipolar moment of CO. We have estimated absorption line strengths for P₃-P₁₈ in band 5 - 0 of ¹²C¹⁶O; these strengths are consistent with a pure vibrational matrix element $\langle 5|p(x)|0\rangle = (3.6 \pm 0.3) \times 10^{-36}$ C m of the electric dipolar moment $p(x)$, a Herman-Wallis coefficient C_0^5 of about -0.1 and a band strength of $(5.1 \pm 1.3) \times 10^{-29}$ m at 293 K.

3. **"Internal Rotation and Spin Conversion of CH₃OH in Solid *Para*-Hydrogen"**, Y.-P. Lee, Y.-J. Wu, R. M. Lees, L.-H. Xu, and J. T. Hougen, submitted to Science.

The quantum solid *para*-hydrogen (*p*-H₂) has recently emerged as a novel host for matrix-isolation spectroscopy; species isolated in *p*-H₂ exhibit spectral lines with widths much smaller than for samples in other inert-gas matrices, and several species have been reported to rotate in *p*-H₂. This high resolution has revealed for the first time the signature of internal rotation for CH₃OH isolated in solid *p*-H₂ and has thereby permitted observation of slow conversion of nuclear spin symmetry from species *E* to *A* in the host matrix. The observed splittings of the *E/A* doublet in the internal-rotation-coupled vibrational modes are qualitatively consistent with those for CH₃OH in the gaseous phase, while the increase in intensity with spin conversion enables unambiguous identification of transitions of the *A* component. Thus, the *p*-H₂ matrix presents a significant new laboratory for the study of large-amplitude vibrational motions and spin conversion processes, providing valuable information to aid understanding of complicated spectral patterns in both the gas phase and in molecular ices.