行政院國家科學委員會專題研究計畫　期中進度報告

以尖端雷射技術研究大氣或燃燒化學重要分子之光譜學,動態學及動力學(1/3)

計畫類別：個別型計畫
計畫編號：NSC94-2113-M-009-017-
執行期間：94年08月01日至95年07月31日
執行單位：國立交通大學應用化學系(所)

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報告類型：精簡報告

處理方式：本計畫可公開查詢

中　華　民　國 95年5月9日

中文摘要

此三年計劃係以尖端雷射技術研究大氣或燃燒化學反應之重要分子的光譜學及其相關氣態反應之化學動態學，共分為七個部分：(1)以步進式時間解析霍氏放光光譜法研究分子光解動態學，測量產物的內能分佈；擬研究的分子有 o-及 p-fluorotoluene；(2)以步進式時間解析霍氏放光光譜法研究雙分子反應的化學動態學，擬研究的反應有：$O(^1D) + CO$；(3)以步進式時間解析霍氏吸收光譜法研究反應中間物之紅外吸收光譜；擬研究的分子有：CH_3SO_2；(4)利用間質隔離法之間格效應，產生新穎分子並以紅外吸收光譜及理論化學計算鑑識之；擬研究的分子有 ONCO；(5)以 $p\text{-}H_2$ 為間質的間質隔離法之新應用之探索；擬探討分子在 $p\text{-}H_2$ 之振轉動光譜及內轉動光譜；(6)利用共振四波混頻光譜法探討自由基之高度預解離能態，擬研究的分子有 HS；(7)利用無膜式衝擊波管研究高溫的化學反應動力學；擬研究 O + CH_3OH 之高溫反應動力學。

Keywords：時間解析霍氏光譜法、動力學、動態學、間質隔離法、共振四波混頻法、衝擊波管

英文摘要

This three-year proposal focuses on spectroscopy, dynamics and kinetics of species important in atmospheric or combustion chemistry; it consists of seven parts: (1) Use step-scan time-resolved Fourier-transform spectroscopy in emission mode to investigate photodissociation dynamics by determining internal energy distributions of photofragments. Species to be studied include o- and p-fluorotoluene; (2) Use step-scan time-resolved Fourier-transform spectroscopy in emission mode to investigate dynamics of bimolecular reactions $O(^1D)$ with CO; (3) Use step-scan time-resolved Fourier-transform spectroscopy in absorption mode to investigate IR absorption of reaction intermediates, such as CO_3SO_2; (4) Use matrix cage effect to produce novel species and to characterize them with IR absorption and quantum chemical calculations. Species of interest are ONCO; (5) Use $p\text{-}H_2$ as a matrix host to explore possible applications of this new matrix host, including rotation of species and internal rotation of species; (6) Use resonant four-wave mixing spectroscopy to investigate predissociative states of HS; (7) Use a diaphragmless shock tube to investigate chemical kinetics of the reaction $O + CH_3OH$ at high temperatures.

Keywords: time-resolved Fourier-transform spectroscopy, kinetics, dynamics, matrix isolation, resonant four-wave mixing, shock-tube

1. **"Molecular elimination in photolysis of *o*- and *p*-fluorotoluene at 193 nm: internal energy of HF determined with time-resolved Fourier-transform spectroscopy"**, S.-K. Yang, S.-Y. Liu, H.-F. Chen, and Y.-P. Lee, **J. Chem. Phys. 123, 224304 (2005)**.

Following photodissociation of *o*-fluorotoluene (*o*-$C_6H_4(CH_3)F$) at 193 nm, rotationally resolved emission spectra of HF($1 \le v \le 4$) in the spectral region 2800 – 4000 cm^{-1} are detected with a step-scan Fourier-transform spectrometer. HF($v \le 4$) shows nearly Boltzmann-type rotational distributions corresponding to a temperature ~1080 K; a short extrapolation from data in the period 0.5 – 4.5 μs leads to a nascent rotational temperature of 1130 ± 100 K with an average rotational energy of 9 ± 2 kJ mol^{-1}. The observed vibrational distribution of ($v = 1$) : ($v = 2$) : ($v = 3$) = 67.6 : 23.2 : 9.2 corresponds to a vibrational temperature of 5330 ± 270 K. An average vibrational energy of $25 \pm {}^{12}_{3}$ kJ mol^{-1} is derived based on the observed population of HF($1 \le v \le 3$) and estimates of the population of HF(v = 0 and 4) by extrapolation. Experiments performed on *p*-fluorotoluene (*p*-$C_6H_4(CH_3)F$) yielded similar results with average rotational energy of 9 ± 2 kJ mol^{-1} and vibrational energy of $26 \pm {}^{12}_{3}$ kJ mol^{-1} for HF. Observed distributions of internal energy of HF in both cases are consistent with that expected for four-center elimination. A modified impulse model taking into account geometries and displacement vectors of transition-states during bond-breaking predicts satisfactorily the rotational excitation of HF. An observed vibrational energy of HF produced from fluorotoluene slightly smaller than that from fluorobenzene might indicate the involvement of seven-membered ring isomers upon photolysis.

2. **"Photodissociation dynamics of formyl fluoride (HFCO) at 193 nm: Branching ratios and distributions of kinetic energy"**, S.-H. Lee, C.-Y. Wu, S.-K. Yang , and Y.-P. Lee, **J. Chem. Phys. 123, 074326 (2005)**.

Following photodissociation of formyl fluoride (HFCO) at 193 nm, we detected products with fragmentation translational spectroscopy utilizing a tunable vacuum ultraviolet beam from a synchrotron for ionization. Among three primary dissociation channels observed in this work, the F-elimination channel HFCO → HCO + F dominates, with a branching ratio ~0.66 and an average release of kinetic energy ~55 kJ mol^{-1}; about 17 % of HCO further decomposes to H + CO. The H-elimination channel HFCO → FCO + H, has a branching ratio ~0.28 and an average release of kinetic energy ~99 kJ mol^{-1}; about 21 % of FCO further decomposes to F + CO. The F-elimination channel likely proceeds via the S_1 surface whereas the H-elimination channel proceeds via the T_1 surface; both channels exhibit moderate barriers for dissociation. The molecular HF-elimination channel HFCO → HF + CO, correlating with the ground electronic surface, has a branching ratio of only ~0.06; the average translational release of 93 kJ mol^{-1}, ~15 % of available energy, implies that the fragments are highly internally excited. Detailed mechanisms of photodissociation are discussed.

3. **"Distribution of internal state of CO from O (^{1}D) + CO determined with time-resolved Fourier-transform spectroscopy"**, H.-F. Chen and Y.-P. Lee, submitted to J. Chem. Phys.

Following collisions of O (^{1}D) with CO, rotationally resolved emission spectra of CO ($1 \leq v \leq 6$) in the spectral region 1800–2350 cm^{-1} were detected with a step-scan Fourier-transform spectrometer. O (^{1}D) was produced by photolysis of O_3 with light from a KrF excimer laser at 248 nm. Upon irradiation of a flowing mixture of O_3 (0.016 Torr) and CO (0.058 Torr), emission of CO ($v \leq 6$) increases with time, reaches a maximum ~10 μs. At the earliest applicable period (2–3 μs), CO shows approximately a bimodal rotational distribution corresponding to temperatures ~8000 K and ~500 K; the proportion of these two components depends on the vibrational level. A short extrapolation from data in the period 2–6 μs leads to a nascent rotational temperature of ~10170 ± 600 K for $v = 1$ and ~1400 ± 40 K for $v = 6$, with an average rotational energy of 33 ± 6 kJ mol^{-1}. Absorption by CO ($v = 0$) in the system interfered with population of low J levels of CO ($v = 1$). The observed vibrational distribution of $(v = 2) : (v = 3) : (v = 4) : (v = 5) : (v = 6) = 1.00: 0.64 : 0.51 : 0.32 : 0.16$ corresponds to a vibrational temperature of 6850 ± 750 K. An average vibrational energy of 40 ± 4 kJ mol^{-1} is derived based on the observed population of CO ($2 \leq v \leq 6$) and estimates of the population of CO ($v = 0$, 1, and 7) by extrapolation. The observed rotational distributions of CO ($1\leq v \leq 3$) are consistent with results of previous experiments and trajectory calculations; data for CO ($4 \leq v \leq 6$) are new.

4. **"Isomers of NCO_2: IR absorption spectra of ONCO in solid Ne"**, Y.-J. Wu and Y.-P. Lee, **J. Chem. Phys. 123, 174301 (2005)**

Irradiation of a Ne matrix sample containing NO and CO near 4 K with an ArF excimer laser at 193 nm yielded new lines at 2045.1 and 968.0 cm^{-1} that were depleted upon secondary photolysis at 308 nm. These lines are assigned to C=O stretching and mixed stretching modes of ONCO, based on results of ^{15}N-, ^{13}C,- and ^{18}O-isotopic experiments and quantum-chemical calculations. These calculations using density-functional theory (B3LYP and PW91PW91/aug-cc-pVTZ) predict five stable isomers of NCO_2: ONCO, NCOO, N-*cyc*-CO_2, CNOO, and *cyc*-CNOO, listed in order of increasing energy. According to B3LYP calculations, ONCO has a *trans* configuration, with bond angles $\angle$ONC $\cong$ 136.3° and $\angle$NCO $\cong$ 160.7°. Calculated vibrational wave numbers, IR intensities, ^{15}N-, ^{13}C,- and ^{18}O-isotopic shifts for ONCO agree satisfactorily with experimental results. ONCO was formed from reaction of CO with NO in its excited state.

5. **"Internal Rotation and Spin Conversion of CH_3OH in Solid *Para*-Hydrogen"**, Y.-P. Lee, Y.-J. Wu, R. M. Lees, L.-H. Xu, and J. T. Hougen, **Science. 311, 365 (2006).**

The quantum solid *para*-hydrogen (*p*-H_2) has recently emerged as a novel host for matrix-isolation spectroscopy; species isolated in *p*-H_2 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*-H_2. This high resolution has revealed for the first time the signature of internal rotation for CH_3OH isolated in solid *p*-H_2 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 CH_3OH in the gaseous phase, while the increase in intensity with spin conversion enables unambiguous identification of transitions of the *A* component. Thus, the *p*-H_2 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.

6. **"The $B^3\Sigma^-$ state of the SO radical"**, C.-P. Liu, N. L. Elliott, C. M. Western, Y.-P. Lee, and R. Colin, **J. Mol. Spectrosc. (accepted).**

Spectra of the $B\ {}^3\Sigma^- – X\ {}^3\Sigma^-$ transition in SO above the first dissociation limit are recorded using degenerate four wave mixing. These spectra are combined with earlier work involving laser induced fluorescence, absorption spectra and Fourier transform emission spectra, to enable a rotational analysis and deperturbation of vibrational levels of the *B* state up to $v' = 16$. Numerous perturbations were noted within the $B\ {}^3\Sigma^-$ state, and the origin of these is discussed. In a number of cases, these perturbations can be attributed to interactions with specific other electronic states of SO, such as $A\ ^3\Pi$, $C\ ^3\Pi$, $d\ ^1\Pi$ and $A''\ ^3\Sigma^+$.

7. **"Experimental and theoretical studies of rate coefficients for the reaction O(^{3}P) + CH$_3$OH at high temperatures"**, C.-W. Lu, S.-L. Chou, Y.-P. Lee, S. Xu, Z. F. Xu, and M. C. Lin, **J. Chem. Phys. 122, 244314 (2005).**

Rate coefficients of the reaction O(^{3}P) + CH_3OH in the temperature range 835−1777 K were determined using a diaphragmless shock tube. O atoms were generated by photolysis of SO_2 with a KrF excimer laser at 248 nm or an ArF excimer laser at 193 nm; their concentrations were monitored via atomic resonance absorption excited by emission from a microwave-discharged mixture of O_2 and He. Rate coefficients determined for the temperature range can be represented by the Arrhenius equation: $k(T) = (2.29\pm0.18)\times10^{-10} \exp[-(4210\pm100)/T]$ cm^3 molecule^{-1} s^{-1}; unless otherwise noted, all listed errors represent one standard deviation in fitting. Combination of these and previous data at lower temperature shows a non-Arrhenius behavior described as the three-parameter equation $k(T) = (2.74\pm0.07)\times10^{-18}\ T^{2.25\pm0.13} \exp[-(1500\pm90)/T]$ cm^3 molecule^{-1} s^{-1}. Theoretical calculations at the B3LYP/6-311+G(3df, 2p) level locate three transition states. Based on the energies computed with CCSD(T)/6-311+G(3df, 2p)//B3LYP/6-311+G(3df, 2p), rate coefficients predicted with canonical variational transition state theory with small curvature tunneling corrections agree satisfactorily with experimental observations. The branching ratios of two accessible reaction channels forming CH_2OH + OH (1a) and CH_3O + OH (1b) are predicted to vary strongly with temperature. At 300 K, reaction (1a) dominates, whereas reaction (1b) becomes more important than reaction (1a) above 1700 K.