

# 行政院國家科學委員會專題研究計畫 成果報告

## 尖端光譜學技術在雷射光化學的應用(3/3)

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計畫主持人：李遠鵬

計畫參與人員：鍾昭宇, 吳宇中, 劉靜萍, 呂志偉, 周柏翰, 廖雪兒

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### 中文摘要

本三年計劃目前共發表 16 篇論文，預計尚有 4-6 篇可發表，成果豐碩。其中在時間解析紅外光譜法方面，完成了  $\text{Cl}_2\text{C}_2\text{O}_4$  在 248nm 及 193nm 光解之研究， $\text{C}_6\text{H}_5\text{F}$ ， $\text{C}_6\text{H}_4(\text{CH}_3)\text{F}$ ， $\text{HFCO}$  在 193 nm 光解之研究， $\text{Cl} + \text{H}_2\text{S}$  及  $\text{Cl} + \text{CH}_3\text{SH}$  之反應動態學研究(以上均利用放光光譜法)，以及  $\text{ClSO}$ ， $\text{ClCS}$ ， $\text{C}_6\text{H}_5\text{SO}_2$  等的瞬態紅外吸收光譜，也完成了 slit-jet 與此光譜法之結合。在四波混頻方面，完成了  $\text{CH}_3\text{S}$  之 A 電子激發態光譜，首次測得 C-H 伸張模之激發及預分解速率對振動模的選擇性，也測量了  $\text{SO}$  的預分解 B 電子態光譜(正分析中)。在 cavity ringdown 方面，完成了  $\text{CO}(5-0)$  之光譜研究發現了 P/R 譜帶的強度反射。

關鍵詞：時間解析霍氏光譜法，反應動態學，同色四波混頻

### 英文摘要

In this 3-year project, we have published 16 papers so far, and expect to have 4-6 more. In the applications of time-resolved Fourier-transform spectroscopy, we have studied photodissociation dynamics of  $\text{Cl}_2\text{C}_2\text{O}_4$  at 248 nm and 193 nm, of  $\text{C}_6\text{H}_5\text{F}$ ,  $\text{C}_6\text{H}_4(\text{CH}_3)\text{F}$ , and  $\text{HFCO}$  at 193 nm, and bimolecular reaction dynamics of  $\text{Cl} + \text{H}_2\text{S}$  and  $\text{Cl} + \text{CH}_3\text{SH}$  (all using emission spectroscopy), and transient absorption spectra of  $\text{ClSO}$ ,  $\text{ClCS}$ , and  $\text{C}_6\text{H}_5\text{SO}_2$ . In degenerate four-wave mixing, we have obtained spectrum of  $\text{CH}_3\text{S}$  that enable as to assign for the first time the C-H stretching mode of the  $\tilde{\text{A}}$  state and the mode selectivity for predissociation. Predissociative levels of the  $\tilde{\text{B}}$  state of  $\text{SO}$  are also recorded; analysis is in progress. We also observed  $\text{CO}(5-0)$  band for the first time with the cavity ringdown technique and found intensity reversal for P/R bands.

Keywords: time-resolved Fourier-transform spectroscopy, reaction dynamics, degenerate four-wave mixing.

1. **"Photolysis of Oxalyl Chloride (ClCO)<sub>2</sub> at 248 nm: Emission of CO ( $v' \leq 3$ ,  $J' \leq 51$ ) detected with time-resolved Fourier-transform spectroscopy"**, C.-Y. Wu, Y.-P. Lee, J. F. Ogilvie, and N. S. Wang, **J. Phys. Chem. A**, 107, 2389 (2003).

Upon photolysis of oxalyl chloride at 248 nm, rotationally resolved emission of CO ( $v \leq 3$ ) in the spectral region 1900-2300  $\text{cm}^{-1}$  was detected with a step-scan time-resolved Fourier-transform spectrometer under nearly collisionless conditions. Boltzmann-like rotational distributions of CO ( $v = 1$  and 2) correspond to temperatures  $\sim 2290 \pm 100$  and  $1910 \pm 130$  K, respectively, with average rotational energy of  $16 \pm 2$   $\text{kJ mol}^{-1}$ ; several lines of CO ( $v = 3$ ) were also observed, but their weak intensity precludes quantitative analysis. The average vibrational energy of CO is estimated to be  $10 \pm 3$   $\text{kJ mol}^{-1}$  according to observed vibrational populations of  $v = 1$  and 2 and that of  $v = 0$  and 3 predicted with surprisal analysis. Combining the average internal energy of CO determined in this work and average translational energies of photofragments Cl, CO, and ClCO determined previously by Suits and coworkers, we derived a revised energy balance. We observed no emission of ClCO near 1880  $\text{cm}^{-1}$ , indicating that ClCO ( $v_1 = 1$ ) decomposes rapidly and that surviving ClCO has little vibrational excitation in the CO stretching mode. Most CO produced from decomposition of ClCO is in its vibrational ground state with small rotational excitation, undetectable with our technique.

2. **"Strengths of absorption features in vibration-rotational band  $v = 6 \leftarrow v = 0$  of  $^{14}\text{N}^{16}\text{O X } ^2\Pi_r$  in the near infrared region"**, Y.-P. Lee, S.-L. Cheah, and J. F. Ogilvie, **Infrared Phys. Tech.** 44, 199 (2003).

The strengths or integrated absorption intensities of individual features in band  $v = 6 \leftarrow v = 0$  of gaseous  $^{14}\text{N}^{16}\text{O X } ^2\Pi_r$  are measured at  $(297.35 \pm 0.4)$  K with spectral resolution 6  $\text{m}^{-1}$ . For unresolved features near band heads in R branches, partition of total intensity enables estimates for each transition, apart from spin-rotation doubling and hyperfine effects. As a sum of these strengths of lines, the strength of the entire band centred near 1 083 606  $\text{m}^{-1}$ , including sub-bands for both  $^2\Pi_{1/2}$  and  $^2\Pi_{3/2}$ , is  $(5.63 \pm 0.28) \times 10^{-27}$  m. We compare measured strengths with those calculated from deduced values of transition moment for electric dipolar moment and Herman–Wallis coefficient.

3. **"Reaction dynamics of Cl + H<sub>2</sub>S: rotational and vibrational distribution of HCl probed with time-resolved Fourier-transform spectroscopy"**, K.-S. Chen, S.-S. Cheng, and Y.-P. Lee, **J. Chem. Phys.** 119, 4229 (2003).

Following laser irradiation of a flowing mixture of S<sub>2</sub>Cl<sub>2</sub> and H<sub>2</sub>S at 308 nm to initiate the reaction of Cl + H<sub>2</sub>S, vibration-rotationally resolved emission spectra of HCl ( $v = 1, 2$ ) in the spectral region 2436–3310  $\text{cm}^{-1}$  are detected with a step-scan time-resolved Fourier-transform spectrometer. The Boltzmann-like rotational distributions of HCl ( $v = 1$ )

and HCl ( $v = 2$ ) yield rotational temperatures that decrease with reaction time; extrapolation to time zero based on data in the range 0.5–4.0  $\mu\text{s}$  yields nascent rotational temperatures of  $1250 \pm 70$  K and  $1270 \pm 120$  K, respectively; an average rotational energy of  $8.3 \pm 1.5$  kJ mol<sup>-1</sup> is determined for HCl ( $v = 1, 2$ ), much greater than a previous report. Observed temporal profiles of the vibrational population of HCl ( $v = 1, 2$ ) are fitted with a kinetic model that includes formation and quenching of HCl ( $v = 1, 2$ ) to yield a branching ratio of  $0.14 \pm 0.01$  for formation of HCl ( $v = 2$ )/HCl ( $v = 1$ ) and a thermal rate coefficient of  $k_I = (3.7 \pm 1.5) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Combining an estimate of the vibrational population of HCl ( $v = 0$ ) based on a surprisal analysis of previous investigations on the reaction Cl + D<sub>2</sub>S, we report a ratio of vibrational distributions of HCl ( $v = 0$ ) : ( $v = 1$ ) : ( $v = 2$ ) = 0.41 : 0.52 : 0.07, which gives an average vibrational energy of  $23 \pm 4$  kJ mol<sup>-1</sup> for HCl. Internal energies, especially rotational energy, of HCl derived with this method is more reliable than with previous techniques; the fractions of available energy going into rotation and vibration of HCl are  $f_r = 0.12 \pm 0.02$  and  $f_v = 0.33 \pm 0.06$ , respectively.

4. **"Highly predissociative levels of CH<sub>3</sub>S ( $A^2A_1$ ) detected with degenerate four-wave mixing"**, C.-P. Liu, Y. Matsuda, and Y.-P. Lee, **J. Chem. Phys.** **119**, 12335 (2003).

Following photodissociation of dimethyl disulfide (CH<sub>3</sub>SSCH<sub>3</sub>) in a supersonic jet with a KrF excimer laser at 248 nm, degenerate four-wave mixing spectra of the  $A^2A_1 \leftarrow X^2E_{3/2}$  transition of CH<sub>3</sub>S in a spectral region 317–377 nm are recorded using a dye laser. Observed features extend to 5020 cm<sup>-1</sup> above the origin, much greater than 1490 cm<sup>-1</sup> for fluorescence spectra and 2979 cm<sup>-1</sup> for fluorescence depletion spectra. In addition to extension to higher members of the known progressions  $3^v$  and  $2^13^v$  associated with C–S stretching ( $\nu_3$ ) and CH<sub>3</sub> umbrella ( $\nu_2$ ) modes, three new progressions  $1^13^v$ ,  $3^v4^1$ , and  $2^13^v4^1$  (or  $1^12^13^v$ ) involving the symmetric CH<sub>3</sub> stretching ( $\nu_1$ ) and asymmetric CH<sub>3</sub> ( $\nu_4$ ) stretching modes of the  $A^2A_1$  state of CH<sub>3</sub>S are tentatively assigned, yielding values of  $\nu_1 = 2966$  cm<sup>-1</sup> and  $\nu_4 = 3006$  cm<sup>-1</sup> that are consistent with theoretical predictions. Vibrational spectral parameters for  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$ , and  $\nu_4$  modes of the  $A^2A_1$  state of CH<sub>3</sub>S are derived.

5. **"Experiments and Calculations on Rate Coefficients for Pyrolysis of SO<sub>2</sub> and the Reaction O + SO at High Temperatures"**, C.-W. Lu, Y.-J. Wu, Y.-P. Lee, R. S. Zhu, and M. C. Lin, **J. Phys. Chem. A.** **107**, 11020 (2003).

Rate coefficients for the pyrolysis of SO<sub>2</sub> in Ar in the temperature range 2188–4249 K were determined using a diaphragmless shock tube. The concentration of O atoms was monitored with resonance absorption. Rate coefficients determined in this work show Arrhenius behavior, with  $k_{Ia}(T) = (4.86 \pm 1.31) \times 10^{-9} \exp [-(50450 \pm 730)/T]$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>; listed errors represent one standard deviation in fitting. These values are consistent with some previous measurements that show a pre-exponential factor and activation energy greater

than other measurements. Theoretical calculations at the G2M(RCC2) level, using geometries optimized with the B3LYP/6-311+G(3df) method, yield energies of transition states and products relative to those of the reactants. Rate coefficients predicted with a microcanonical variational RRKM theory agree well with experimental observations; contributions from electronically excited states of SO<sub>2</sub> are significant. Rate coefficients for the recombination O + SO → SO<sub>2</sub> are predicted to decrease with temperature with  $k_{10a}(T) = (4.82 \pm 0.05) \times 10^{-31} (T/298)^{-2.17 \pm 0.03} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for the temperature range 298–3000 K. In some experiments S atoms were monitored with resonance absorption. With detailed chemical modeling, we found that S atoms were mainly produced from the secondary reaction O + SO → S + O<sub>2</sub> rather than from direct pyrolysis of SO<sub>2</sub> or from further pyrolysis of the SO product. Rate coefficients for this secondary reaction, determined to be  $k_{10b}(T) = (3.0 \pm 0.3) \times 10^{-11} \exp [-(6980 \pm 280)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , agree closely with the theoretically predicted value comprising three product-channels via one triplet and two singlet SOO intermediates.

6. **"Reaction dynamics of Cl + CH<sub>3</sub>SH: rotational and vibrational distributions of HCl probed with time-resolved Fourier-transform spectroscopy"**, S.-S. Cheng, Y.-J. Wu, and Y.-P. Lee, **J. Chem. Phys.** 120, 1792 (2004).

Rotationally resolved infrared emission spectra of HCl( $v = 1-3$ ) in the reaction of Cl + CH<sub>3</sub>SH, initiated with radiation from a laser at 308 nm, are detected with a step-scan Fourier-transform spectrometer. Observed rotational temperature of HCl( $v = 1-3$ ) decreases with duration of reaction due to collisional quenching; a short extrapolation to time zero based on data in the range 0.25–4.25 μs yields a nascent rotational temperature of  $1150 \pm 80$  K. The rotational energy averaged for HCl( $v = 1-3$ ) is  $8.2 \pm 0.9 \text{ kJ mol}^{-1}$ , yielding a fraction of available energy going into rotation of HCl,  $\langle f_r \rangle = 0.10 \pm 0.01$ , nearly identical to that of the reaction Cl + H<sub>2</sub>S. Observed temporal profiles of the vibrational population of HCl( $v = 1-3$ ) are fitted with a kinetic model of formation and quenching of HCl( $v = 1-3$ ) to yield a branching ratio  $(68 \pm 5) : (25 \pm 4) : (7 \pm 1)$  for formation of HCl( $v = 1$ ) : ( $v = 2$ ) : ( $v = 3$ ) from the title reaction and its thermal rate coefficient  $k_{2a} = (2.9 \pm 0.7) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Considering possible estimates of the vibrational population of HCl( $v = 0$ ) based on various surprisal analyses, we report an average vibrational energy  $36 \pm 6 \text{ kJ mol}^{-1}$  for HCl. The fraction of available energy going into vibration of HCl is  $\langle f_v \rangle = 0.45 \pm 0.08$ , significantly greater than a value  $\langle f_v \rangle = 0.33 \pm 0.06$  determined previously for Cl + H<sub>2</sub>S. Reaction dynamics of Cl + H<sub>2</sub>S and Cl + CH<sub>3</sub>SH are compared; the adduct CH<sub>3</sub>S(Cl)H is likely more transitory than the adduct H<sub>2</sub>SCl.

7. **"Detection of ClSO with time-resolved Fourier-transform infrared absorption spectroscopy"**, L.-K. Chu and Y.-P. Lee, **J. Chem. Phys.** 120, 3179 (2004).

ClSO was produced as an intermediate upon irradiating a flowing mixture of Cl<sub>2</sub>SO and

Ar with a KrF excimer laser at 248 nm. A step-scan Fourier-transform infrared spectrometer coupled with a small multipass absorption cell was employed to detect time-resolved absorption spectrum of ClSO. A transient spectrum in the region 1120–1200  $\text{cm}^{-1}$ , which diminished on prolonged reaction, is assigned to the S–O stretching ( $\nu_1$ ) mode of ClSO. A spectrum with a resolution of 0.3  $\text{cm}^{-1}$  partially reveals rotational structure with the Q-branch at 1162.9  $\text{cm}^{-1}$ . Calculations with density-functional theory (B3LYP/aug-cc-pVTZ) predict the geometry, vibrational and rotational parameters of ClSO. An IR absorption spectrum of ClSO simulated based on predicted rotational parameters agrees satisfactorily with experimental results. ClSO produced from photolysis of  $\text{Cl}_2\text{SO}$  at 248 nm is internally hot.

8. **"Photolysis of oxalyl chloride ( $\text{ClCO}$ )<sub>2</sub> at 193 nm : Emission of  $\text{CO}(\nu \leq 6, J \leq 60)$  detected with time-resolved Fourier-transform spectroscopy", C.-Y. Wu, Y.-P. Lee, and N. S. Wang, *J. Chem. Phys.* **120**, 6957 (2004).**

Upon photolysis of oxalyl chloride at 193 nm, time-resolved and rotationally resolved emission of CO ( $\nu \leq 6, J \leq 60$ ) in the spectral region 1850–2350  $\text{cm}^{-1}$  was detected with a step-scan Fourier-transform spectrometer under nearly collisionless conditions. Boltzmann-type rotational distributions of CO correspond to temperatures  $3520 \pm 110$  ( $\nu = 1$ ) to  $2300 \pm 610$  K ( $\nu = 6$ ), with an average rotational energy of  $23 \pm 2$   $\text{kJ mol}^{-1}$ . The average vibrational energy of CO is estimated to be  $26 \pm 4$   $\text{kJ mol}^{-1}$  according to observed vibrational populations of  $\nu = 1$ –6 and that of  $\nu = 0$  predicted with a surprisal analysis. Combining the average internal energy of CO determined in this work and average translational energies of photofragments Cl and CO determined previously by Hemmi and Suits, we propose a four-body dissociation mechanism producing one pair of translationally rapid and internally excited CO and one pair of translationally rapid Cl, each with similar energies, to account for the energy balance. Formation of translationally slow ClCO, Cl, and CO reported previously by Hemmi and Suits might be rationalized with a second channel involving emission of electronically excited intermediates. We observed no emission of ClCO near 1880  $\text{cm}^{-1}$ , indicating that surviving ClCO has little vibrational excitation in the C–O stretching mode.

9. **"Experimental and theoretical investigations of rate coefficients of the reaction  $\text{S}({}^3\text{P}) + \text{O}_2$  in the temperature range 298-878 K", C.-W. Lu, Y.-J. Wu, Y.-P. Lee, R. S. Zhu, and M. C. Lin, *J. Chem. Phys.* **121**, 8271, (2004).**

Rate coefficients of the reaction  $\text{S} + \text{O}_2$  with Ar under 50 Torr in the temperature range 298–878 K were determined with the laser photolysis technique. S atoms were generated by photolysis of OCS with a KrF excimer laser at 248 nm; their concentration was monitored via resonance fluorescence excited by atomic emission of S produced from microwave-discharged  $\text{SO}_2$ . Our measurements show that  $k(298 \text{ K}) = (1.92 \pm 0.29) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , in satisfactory agreement with previous reports. New data determined for 505–878 K

show non-Arrhenius behavior; combining our results with data reported at high temperatures, we derive an expression  $k(T) = (9.02 \pm 0.27) \times 10^{-19} T^{2.11 \pm 0.15} \exp[(730 \pm 120)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $298 \leq T/\text{K} \leq 3460$ . Theoretical calculations at the G2M(RCC2) level, using geometries optimized with the B3LYP/6-311+G(3df) method, yield energies of transition states and products relative to those of the reactants. Rate coefficients predicted with multichannel RRKM calculations agree satisfactorily with experimental observations; the reaction channel via  $\text{SOO}({}^1\text{A}')$  dominates at  $T < 500 \text{ K}$ , whereas channels involving formation of  $\text{SOO}({}^3\text{A}'')$  followed by isomerization to  $\text{SO}_2$  before dissociation, and formation of  $\text{SOO}({}^1\text{A}'')$  followed by direct dissociation, become important at high temperatures, accounting for the observed rapid increase in rate coefficient.

10. **"Molecular elimination in photolysis of fluorobenzene at 193 nm: internal energy of HF determined with time-resolved Fourier-transform spectroscopy"**, C.-Y. Wu, Y.-J. Wu, and Y.-P. Lee, **J. Chem. Phys.** **121**, 8792, (2004).

Following photodissociation of fluorobenzene ( $\text{C}_6\text{H}_5\text{F}$ ) at 193 nm, rotationally resolved emission spectra of  $\text{HF}(1 \leq v \leq 4)$  in the spectral region  $2800\text{--}4000 \text{ cm}^{-1}$  are detected with a step-scan Fourier-transform spectrometer. In the period  $0.1\text{--}1.1 \mu\text{s}$  after photolysis,  $\text{HF}(v \leq 4)$  shows similar Boltzmann-type rotational distributions corresponding to a temperature  $\sim 1830 \text{ K}$ ; a short extrapolation from data in the period  $0.1\text{--}4.1 \mu\text{s}$  leads to a nascent rotational temperature of  $1920 \pm 140 \text{ K}$  with a average rotational energy of  $15 \pm 3 \text{ kJ mol}^{-1}$ . The observed vibrational distribution of  $(v = 1) : (v = 2) : (v = 3) : (v = 4) = (60 \pm 7) : (24 \pm 3) : (10.5 \pm 1.2) : (5.3 \pm 0.5)$  corresponds to a vibrational temperature of  $6400 \pm 180 \text{ K}$ . An average vibrational energy of  $33 \pm 3 \text{ kJ mol}^{-1}$  is derived based on the observed population of  $\text{HF}(1 \leq v \leq 4)$  and an estimate of the population of  $\text{HF}(v = 0)$  by extrapolation. The observed internal energy distribution of HF is consistent with that expected for the four-center ( $\alpha, \beta$ ) elimination channel. A modified impulse model taking into account geometries and displacement vectors of transition-states during bond breaking predicts satisfactorily the rotational excitation of HF. We also compare internal energies of HF observed in this work with those from photolysis of vinyl fluoride ( $\text{CH}_2\text{CHF}$ ) and 2-chloro-1,1-difluoroethene ( $\text{CF}_2\text{CHCl}$ ) at 193 nm.

11. **"Photodissociation dynamics of vinyl chloride investigated with a pulsed slit-jet and time-resolved Fourier-transform spectroscopy"**, M. Bahou and Y.-P. Lee, **Aus. J. Chem.** **57**, 1161 (2004).

Following photodissociation of vinyl chloride seeded in a He supersonic jet at 193 nm, rotationally resolved infrared emission of  $\text{HCl}(v)$  are recorded to yield nascent rotational and vibrational distributions. Preliminary results show that the rotational distribution of  $\text{HCl}$  free from rotational quenching deviates slightly from Boltzmann-type distribution and agrees well

with trajectory calculations; a portion of the low- $J$  component observed previously in a flow system is attributed to quenching. The implications for photodissociation dynamics are discussed.

**12. "Two-color resonant four-wave spectroscopy of highly predissociated levels in the  $\tilde{A}^2A_1$  state of  $CH_3S$ ", C.-P. Liu, S. A. Reid, and Y.-P. Lee, *J. Chem. Phys.* **122**, 124313 (2005).**

We report results of two-color resonant four-wave mixing experiments on highly predissociated levels of the methylthio (or thiomethoxy) radical,  $CH_3S$ , in its first excited electronic state  $\tilde{A}^2A_1$ . Following photolysis of jet-cooled dimethyl disulfide at 248 nm, the spectra were measured with a hole-burning scheme in which the probe laser excited specific rotational transitions in band 3<sup>3</sup>. The spectral simplification afforded by the two-color method allows accurate determination of line positions and homogeneous line widths, which are reported for the C–S stretching states 3<sup>v</sup> ( $v = 3–7$ ) and combination states 1<sup>1</sup>3<sup>v</sup> ( $v = 0–2$ ), 2<sup>1</sup>3<sup>v</sup> ( $v = 3–6$ ), and 1<sup>1</sup>2<sup>1</sup>3<sup>v</sup> ( $v = 0, 1$ ) involving the symmetric  $CH_3$  stretching ( $\nu_1$ ) mode and the  $CH_3$  umbrella ( $\nu_2$ ) mode. The spectra show pronounced mode specificity, as the homogeneous line width of levels with similar energies varies up to 2 orders of magnitude;  $\nu_3$  is clearly a promoting mode for dissociation. Derived vibrational wave numbers  $\omega_1'$ ,  $\omega_2'$ , and  $\omega_3'$  of the  $\tilde{A}$  state agree satisfactorily with *ab initio* predictions.

**13. "Experimental and theoretical studies of rate coefficients for the reaction  $O(^3P) + CH_3OH$  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  $O(^3P) + CH_3OH$  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:  $k(T) = (2.29 \pm 0.18) \times 10^{-10} \exp [-(4210 \pm 100)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ; 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  $k(T) = (2.74 \pm 0.07) \times 10^{-18} T^{2.25 \pm 0.13} \exp [-(1500 \pm 90)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . 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.

**14. "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  $\text{HFCO} \rightarrow \text{HCO} + \text{F}$  dominates, with a branching ratio  $\sim 0.66$  and an average release of kinetic energy  $\sim 55 \text{ kJ mol}^{-1}$ ; about 17 % of HCO further decomposes to  $\text{H} + \text{CO}$ . The H-elimination channel  $\text{HFCO} \rightarrow \text{FCO} + \text{H}$ , has a branching ratio  $\sim 0.28$  and an average release of kinetic energy  $\sim 99 \text{ kJ mol}^{-1}$ ; about 21 % of FCO further decomposes to  $\text{F} + \text{CO}$ . 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  $\text{HFCO} \rightarrow \text{HF} + \text{CO}$ , correlating with the ground electronic surface, has a branching ratio of only  $\sim 0.06$ ; the average translational release of  $93 \text{ kJ mol}^{-1}$ ,  $\sim 15$  % of available energy, implies that the fragments are highly internally excited. Detailed mechanisms of photodissociation are discussed.

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

We have recorded extremely weak absorption in overtone band 5 – 0 of  $^{12}\text{C}^{16}\text{O X } ^1\Sigma^+$  near  $0.96 \mu\text{m}$  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  $P_3$ – $P_{18}$  in band 5 – 0 of  $^{12}\text{C}^{16}\text{O}$ ; these strengths are consistent with a pure vibrational matrix element  $\langle 5|p(x)|0\rangle = (3.6 \pm 0.3) \times 10^{-36} \text{ C m}$  of the electric dipolar moment  $p(x)$ , a Herman-Wallis coefficient  $C_0^5$  of about  $-0.1$  and a band strength of  $(5.1 \pm 1.3) \times 10^{-29} \text{ m}$  at 293 K.

**16. "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.** (in press)

Following photodissociation of *o*-fluorotoluene (*o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)F) at 193 nm, rotationally resolved emission spectra of HF( $1 \leq v \leq 4$ ) in the spectral region 2800 – 4000 cm<sup>-1</sup> are detected with a step-scan Fourier-transform spectrometer. HF( $v \leq 4$ ) shows nearly Boltzmann-type rotational distributions corresponding to a temperature ~1080 K; a short extrapolation from data in the period 0.5 – 4.5  $\mu$ s leads to a nascent rotational temperature of  $1130 \pm 100$  K with an average rotational energy of  $9 \pm 2$  kJ mol<sup>-1</sup>. The observed vibrational distribution of ( $v = 1$ ) : ( $v = 2$ ) : ( $v = 3$ ) = 67.6 : 23.2 : 9.2 corresponds to a vibrational temperature of  $5330 \pm 270$  K. An average vibrational energy of  $25 \pm \frac{12}{3}$  kJ mol<sup>-1</sup> is derived based on the observed population of HF( $1 \leq v \leq 3$ ) and estimates of the population of HF( $v = 0$  and 4) by extrapolation. Experiments performed on *p*-fluorotoluene (*p*-C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)F) yielded similar results with average rotational energy of  $9 \pm 2$  kJ mol<sup>-1</sup> and vibrational energy of  $26 \pm \frac{12}{3}$  kJ mol<sup>-1</sup> 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.