Predissociation Dynamics of the $A^2\Sigma^+$ State of SH Radical

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Introduction

Mercapto radical (SH):
- The SH radical plays an important role in atmospheric sulfur cycle, fossil fuel combustion, and interstellar medium.
- Photo-predissociation of SH via the $A^2\Sigma^+$ state is a complicated process involving various non-adiabatic interactions.
- Predissociation of $A^2\Sigma^+$ results from its crossings and spin-orbit couplings with three repulsive states ($^4\Sigma^-$, $^2\Sigma^-$, and $^4\Pi$), and leads to the $H(^2S) + S(^3P_J)$ products

K. Freed and coworkers, *J. Chem. Phys.* **114**, 5537 (2001)
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Photodissociation dynamics of the SH radical is studied via several rovibrational levels (v'= 0-6) in the $A^2\Sigma^+$ state using the high-n Rydberg atom time-of-flight (HRTOF) technique. A simulation program was used to predict the recoil photofragment angular distributions as a function of the transition energy, rotational level, rotation constant, and dissociation time scale.

P. Houston and coworkers. *J. Chem. Phys.* **125**, 13, 133316 (2006)
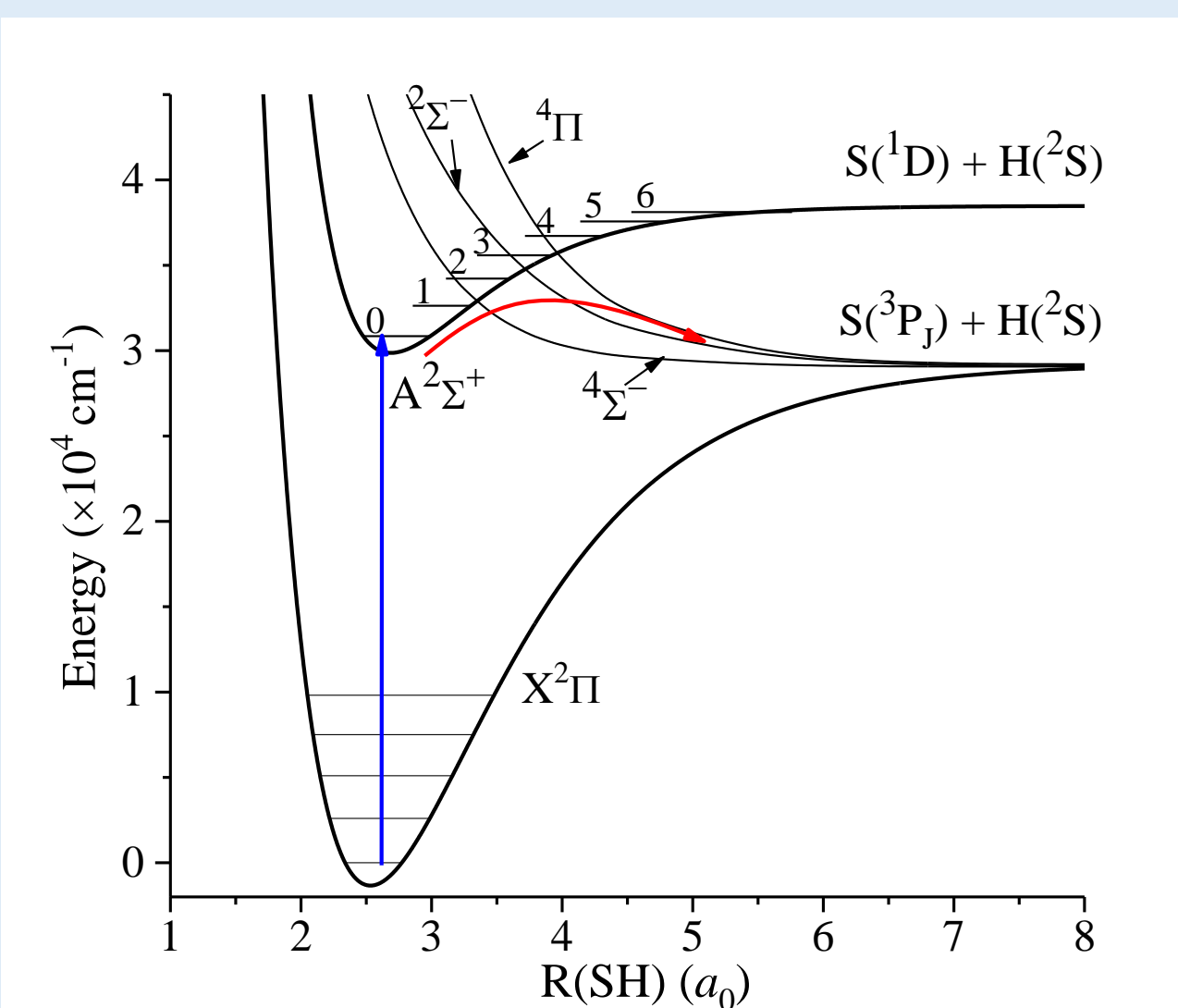
The relative energy levels of the fine structure and electronic states of the S atom are listed below:

$S(^3P_2)$	0.000 cm⁻¹
$S(^3P_1)$	396.055 cm⁻¹
$S(^3P_0)$	573.640 cm⁻¹
$S(^1D)$	9238.609 cm⁻¹

NIST Atomic spectra Database Levels Data

H. Sun and coworkers, *Chem. Phys. Lett.* **194**, 485 (1992)
M. Manna, *Int. J. Quantum Chem., Quantum Chem. Symp.* **29**, 577 (1995)
F. Ornellas and coworkers, *J. Chem. Phys.* **115**, 2178 (2001)

Method and Experimental Setup
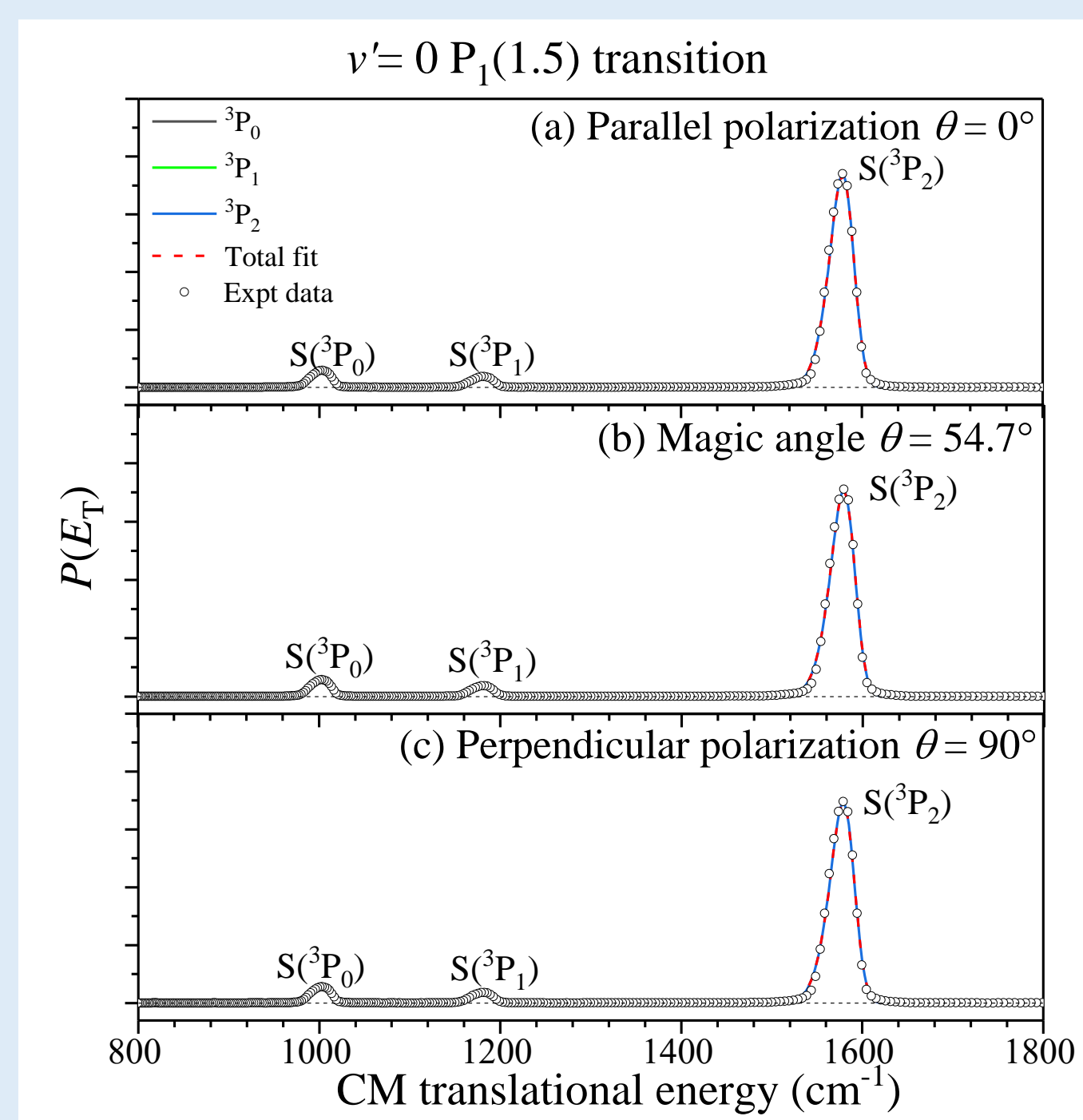
High-n Rydberg atom time-of-flight technique
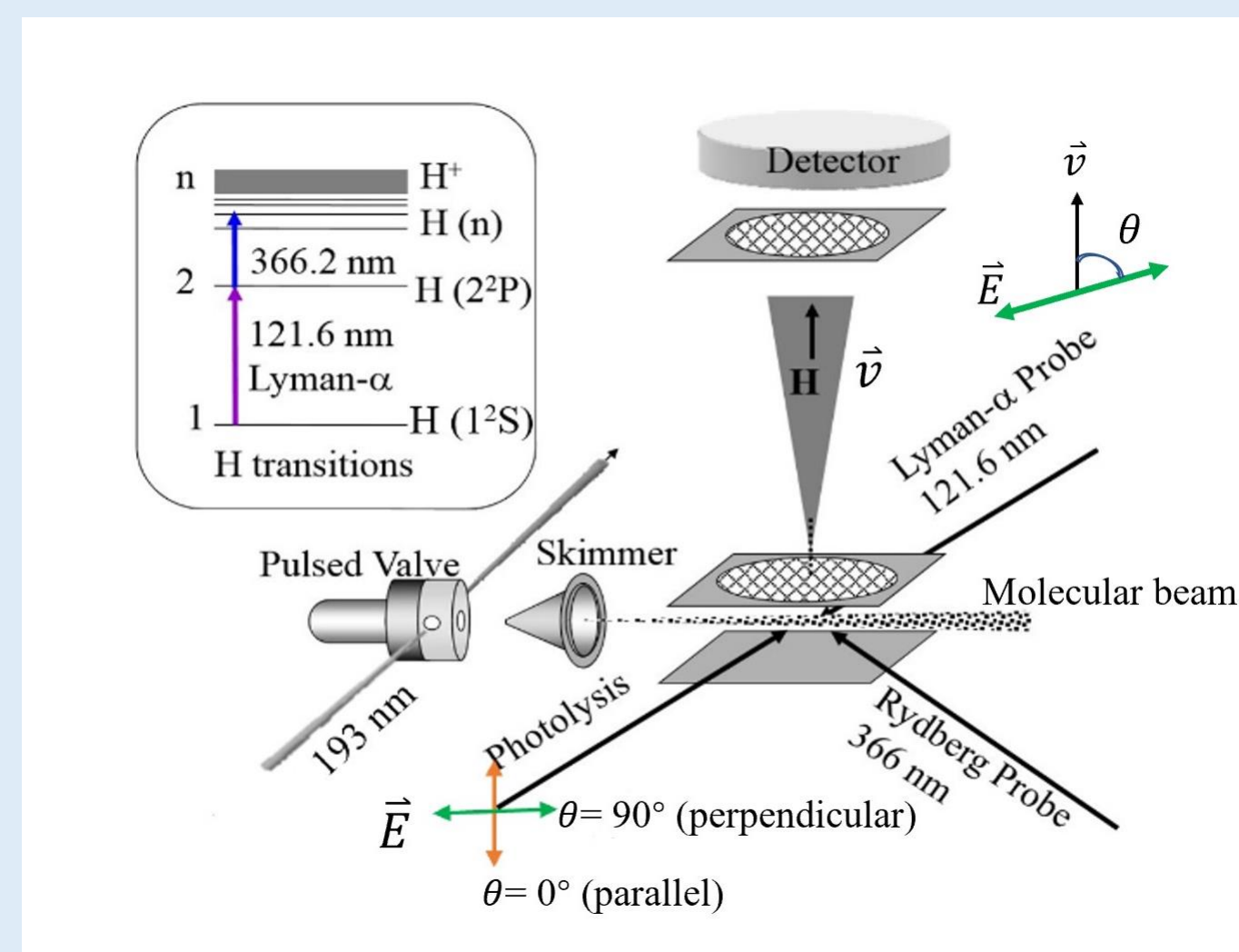
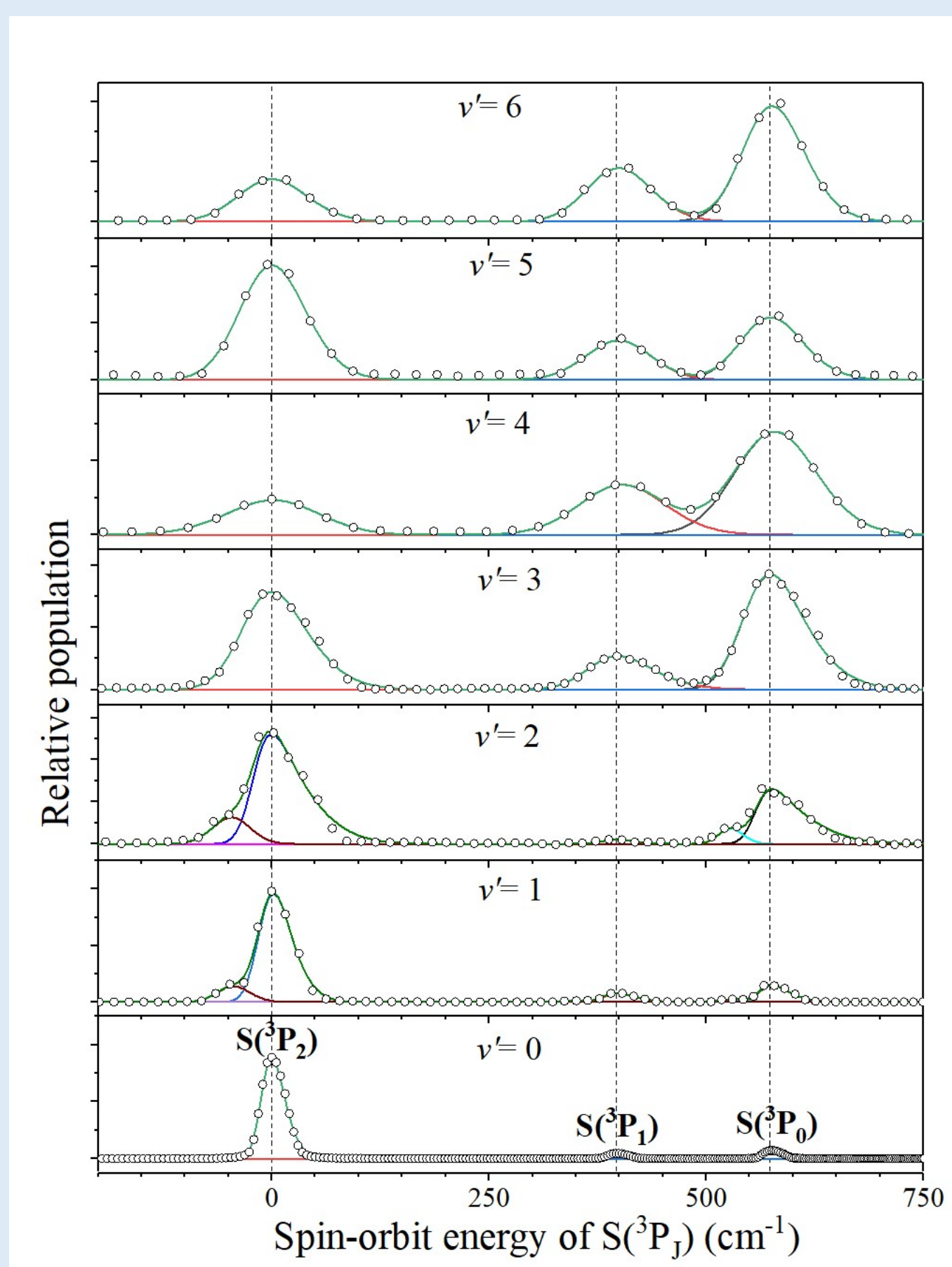K. Welge and coworkers, *J. Chem. Phys.* **92**, 7027 (1990)

SH radical production:

$$H_2S + 193\ nm \rightarrow SH + H$$

Results

Center-of-mass H + $S(^3P_J)$ product translational energy distributions, $P(E_T)$s, from predissociation of SH ($A^2\Sigma^+$, v' = 0, N' = 0, J' = 0.5) via the $P_1(1.5)$ transition. The $S(^3P_J)$ product peaks are deconvoluted, and the product branching ratios and anisotropy parameters (β) are calculated.

Relative population of H + $S(^3P_J)$ products as a function of the spin-orbit energy of $S(^3P_J)$, obtained from the magic angle $P(E_T)$s from predissociation of SH ($A^2\Sigma^+$, v'= 0-6) via the $P_1(1.5)$ transition (or near that). The relative population of $S(^3P_{J=2,1,0})$ products change significantly as v' varies, indicating different predissociation dynamics.
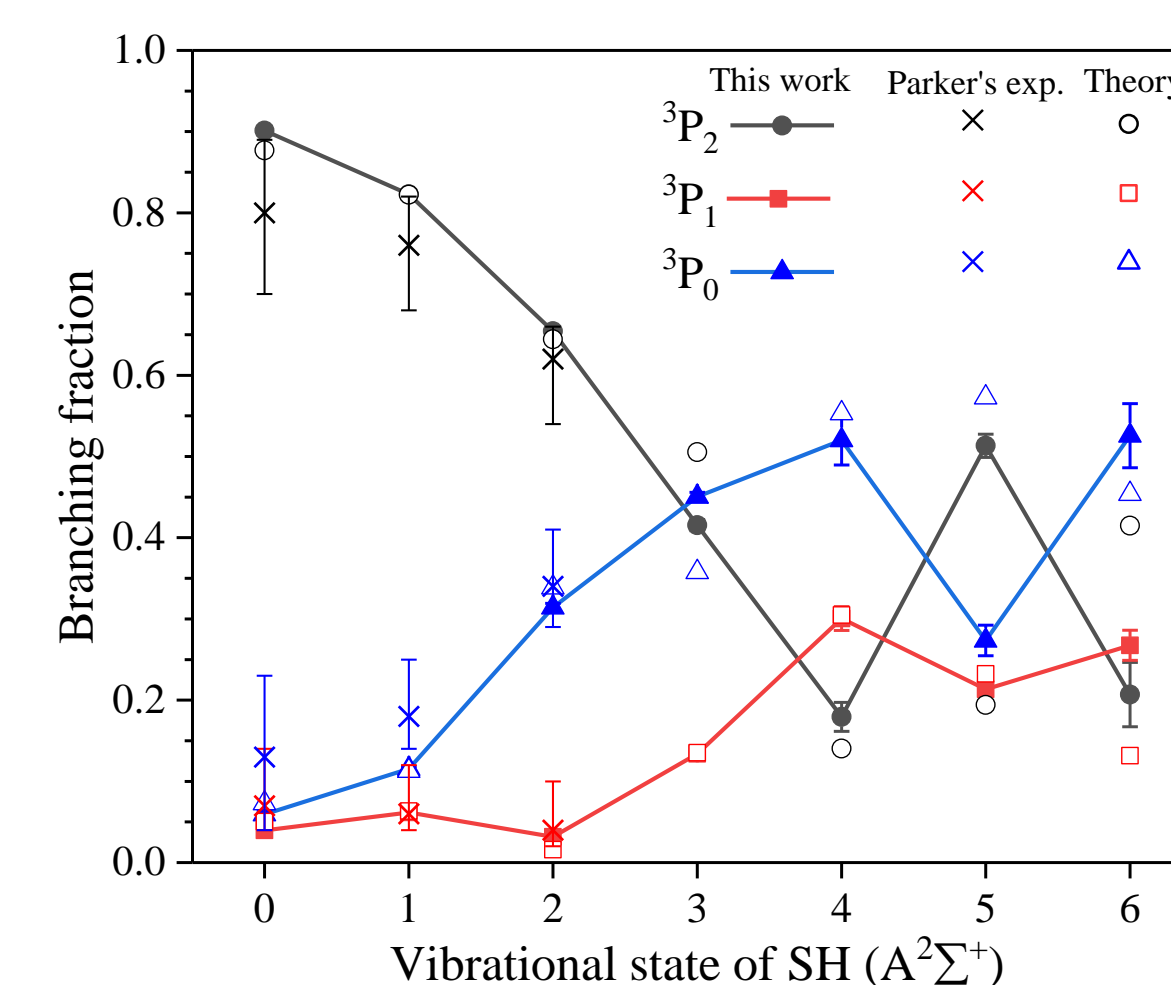

Experimental fine structure branching fractions of $S(^3P_{J=2,1,0})$ fragments from the predissociation of SH $A^2\Sigma^+$ (v'= 0-6) states compared with previous work. In addition to matching Parker's results for v'= 0-2 using velocity map imaging[1], our measurements of lower levels (v'= 0-4) are also in excellent agreement with the close-coupling quantum calculations by Alexander, despite the significant deviation at v'= 5-6[2]. The $A^2\Sigma^+$ v'= 0 predisssociates predominantly via adiabatically coupling to the $^4\Sigma^-$ state. As v' increases, all the three repulsive states ($^4\Sigma^-$, $^2\Sigma^-$, and $^4\Pi$) are involved in the dissociation pathways, and interferences of these dissociation pathways influence the $S(^3P_J)$ fine-structure distributions.

[1] D. H. Parker and coworkers, *J. Chem. Phys.* **130**, 034307 (2009)
[2] M. H. Alexander (2020, January). Spin-Orbit Branching in the Predissociation of SH and OH, presented at the workshop of The Molecular Underpinnings of Astrophysics, Telluride, CO.

$A^2\Sigma^+$		N'	β_{exp}				β_{cal}
			$^3P_2$	$^3P_1$	$^3P_0$	Weighted Average	
v'= 0	$P_1(1.5)$	0	-0.03±0.05	0.01±0.05	-0.05±0.05	-0.03±0.05	0.00
	$Q_1(1.5)$, $^QP_{21}(1.5)$	1	-0.10±0.12	-0.08±0.13	-0.10±0.12	-0.10±0.11	-0.67
	$R_1(1.5)$, $^RQ_{21}(1.5)$	2	0.31±0.06	0.26±0.08	0.26±0.09	0.30±0.06	0.50
v'= 1	$P_1(1.5)$	0	-0.03±0.04	-0.05±0.07	-0.03±0.08	-0.03±0.04	0.02
	$Q_1(1.5)$, $^QP_{21}(1.5)$	1	-0.48±0.11	-0.44±0.09	-0.44±0.11	-0.47±0.09	-0.87
	$R_1(1.5)$, $^RQ_{21}(1.5)$	2	0.26±0.09	0.15±0.12	0.21±0.10	0.25±0.07	0.35
v'= 2	$P_1(1.5)$	0	-0.19±0.08	-0.18±0.09	-0.18±0.07	-0.19±0.05	0.00
	$Q_1(1.5)$, $^QP_{21}(1.5)$	1	-0.66±0.04	-0.63±0.10	-0.65±0.04	-0.66±0.03	-0.85
	$R_1(1.5)$, $^RQ_{21}(1.5)$	2	0.21±0.08	0.14±0.10	0.21±0.08	0.21±0.06	0.17

Experimental measurements of the anisotropy parameters β for predissociation of SH $A^2\Sigma^+$ (v'= 0, 1, and 2), which agree with Parker's work. Comparing the results with calculated β from *Betaofnu* program, the theoretical model gives good predictions, except some discrepancies at the $Q_1(1.5)$ transition where a high degree of alignment is expected.

D. H. Parker and coworkers, *J. Chem. Phys.* **130**, 034307 (2009)
Betaofnu program, P. Houston and coworkers. *J. Chem. Phys.* **125**, 13, 133316 (2006)
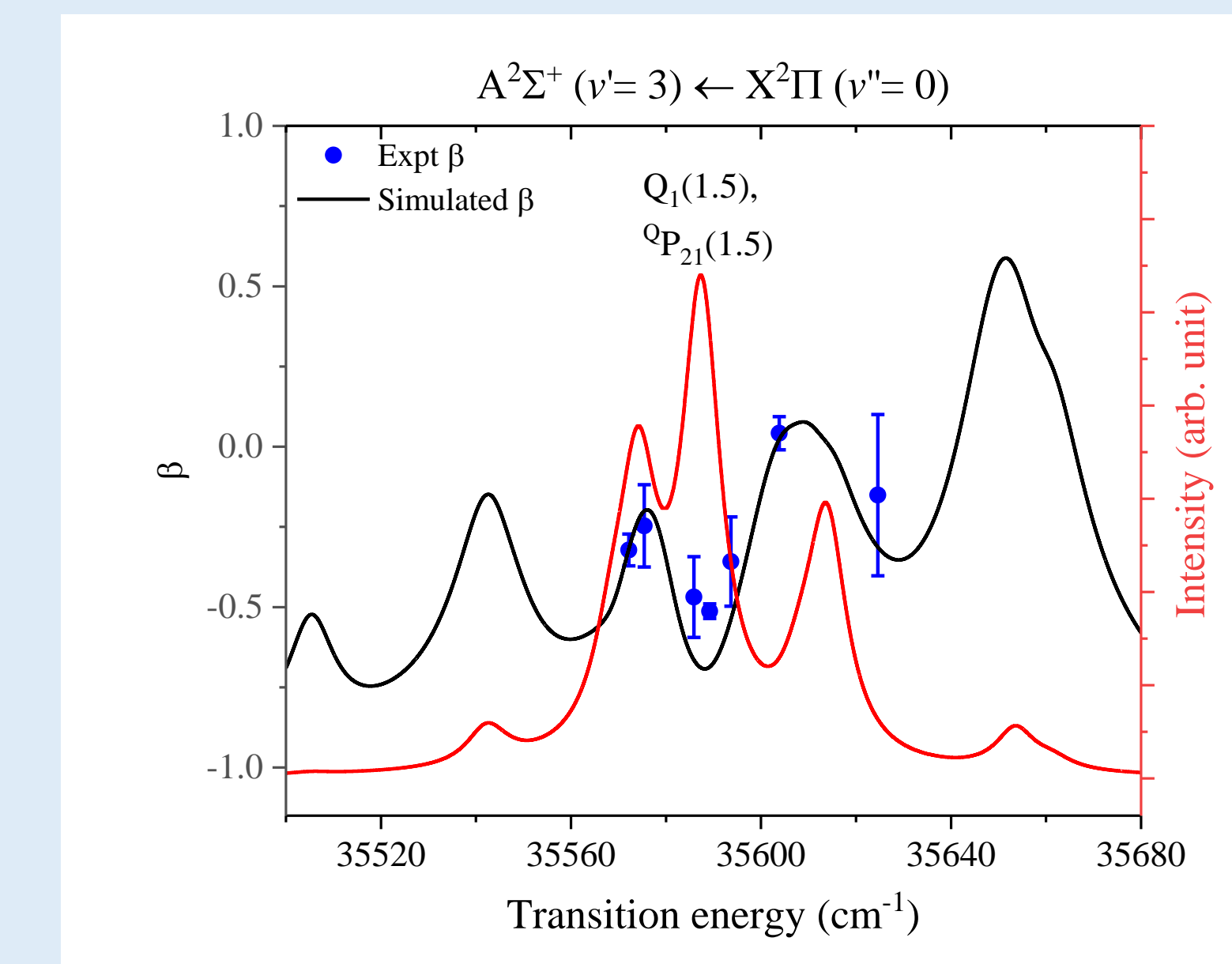
Simulated absorption spectrum and β parameter for the predissociation of SH $A^2\Sigma^+$ (v'= 3), along with the experimental results for β. As the signal peaks are broad for $v'≥3$, the rotational contributions can not be resolved.

The reduced magnitude of β values of the $Q_1(1.5)$ transition at v'= 0-1 might result from the longer predissociation time scale, allowing more time for depolarization. As the predissociation time of the $A^2\Sigma^+$ state decreases at higher v' levels, the depolarization reduces.

Summary

The photodissociation dynamics of SH radical is studied via several rovibrational levels (v'= 0-6) in the $A^2\Sigma^+$ state using the high-n Rydberg atom time-of-flight (HRTOF) technique.

The spin-orbit branching fractions of the $S(^3P_{J=2,1,0})$ products are measured, and the branching ratios depend on the vibrational levels. The measurements are in excellent agreement with the theoretical predications for v'= 0-4 levels. The SH $A^2\Sigma^+$ v'= 0 predisssociates predominantly via adiabatically coupling to the $^4\Sigma^-$ state. As v' increases, all the three repulsive states ($^4\Sigma^-$, $^2\Sigma^-$, and $^4\Pi$) are involved in the dissociation pathways, and interferences of these dissociation pathways influence the $S(^3P_J)$ fine-structure distributions.

The H-atom product angular distributions of the H + $S(^3P_J)$ product channels are measured at various transitions of $A^2\Sigma^+$, and the magnitude of alignment is affected by the excited state lifetimes. The angular distributions are consistent with optical alignment in the initial excitation and the subsequent depolarization.

Acknowledgement