<u>Spin-polarized hydrogen</u> isotopes from <u>UV molecular photodissociation</u>, and nuclear-spin-polarized molecules from <u>IR rovibrational excitation</u> followed by



hyperfine beating





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**Optical Methods of SPH production** 

• Optical-pumping Limited mainly to alkali atoms



Rb polarization can approach 100%

Closed Transition lifetime ~20 ns

795 nm

#### Direct Optical Pumping of H at 121.6 nm



Spin-exchange Optical Pumping of SPH

• Optical-pumping Limited mainly to alkali atoms (and noble gases and SPH via Spin-exchange optical pumping)



#### **Direct Optical Pumping of molecules**



Internuclear separation

Optical Pumping in molecules not possible:

- 1) UV transitions are open
- 2) IR transitions go to states with long lifetimes (ms)

Despite failure of optical pumping, we show how SINGE-PHOTON EXCITATION can still make SPH with up to 100% polarization

We will consider 2 methods:1) UV excitation (photodissociation)2) IR (rovibrational) excitation

... followed by hyperfine beating to polarize the nuclei

#### **Pulsed IR rovibrational excitation**

Polarizing molecular rotation (instead of electronic spin):



T. Peter Rakitzis, Phys. Rev. Lett. 94, 83005 (2005).

#### Pulsed Excitation of H<sub>2</sub>



#### Pump-Probe (IR-UV) setup for measurement of hyperfine beating



#### Pulsed Excitation of HCI





## Hyperfine beating in HD and D<sub>2</sub>



#### **Conclusions I**

1) Rovibrational excitation of diatomic molecules, to produce rotational Polarization, which is then transferred to the nuclear spin through Hyperfine beating, has been demonstrated for HCl, HD,  $D_2$ , and calculated for HF/DF.

2) Appropriate lasers IR exist with  $>10^{22}$  photons/s.

3) Large production rates of spin-polarized nuclei may be possible.Perhaps spin-polarized molecules can be stored at surfaces.



#### <u>Advantages</u>

- high-density (stable molecules, e.g. DI, DF, at high pressure)
- not limited to alkali gases
- can produce highly polarized photofragments
- short timescales of production (ns-fs)
- Transitions in UV-IR, where powerful lasers exist (> $10^{22}$  phot/s)
- Efficient: 1 photon  $\rightarrow$  1 polarized D

## <u>Can the photon helicity be transferred</u> <u>to atoms via photodissociation?</u>



$$S_{photon} = 1$$
  
m = +1  
Circularly Polarized Light

$$S_{\rm H} = 1/2$$
  
 $m_{\rm H} = \pm 1/2$   
Circularly Polarized Matter

## **General Idea**

Adiabatic correlation of molecular electronic states to specific atomic m states van Brunt and Zare, J. Chem. Phys. 48, 4304 (1968).

$$AB(\Omega_g) + hf \rightarrow AB(\Omega_i) \rightarrow A(J_A, m_A) + B(J_B, m_B)$$









A Search of the Literature Shows:





All channels via (predominantly) Perpendicular Transitions ( $\Delta \Omega = \pm 1$ )!

[1] J. Zhang, M. Dulligan, C. Wittig, J. Chem. Phys. 107, 1403 (1997)
[2] R. Baumfalk, U. Buck, C. Frischkorn, N. Nahler, L. Hüwel, J. Chem. Phys. 111, 2595 (1999)

## Now, do experiment to detect SPH

# **<u>BUT</u>**, we didn't know how to detect the SPH with lasers.

#### For H, ionization schemes are not

#### significiantly sensitive to polarization

(spin-orbit splitting much smaller than Doppler spread, and coupling time much slower than ionization time)

## "Temporary" solution:

Detect Cl or Br cofragment polarization, andinfer H polarization from conservation ofangular momentumXH

# Slice Imaging Spectrometer





## <u>HC1 $\rightarrow$ H + Cl (J=1/2)</u>

RR



 $\frac{I_{RCP}}{I_{LCP}} = 1.8 \pm 0.2$ 

RL





## <u>HCl $\rightarrow$ H + <u>Cl (J=3/2)</u></u>

RR



 $\frac{I_{RCP}}{I_{LCP}} = 1.4 \pm 0.2$ 





### CI polarization from HCI photodissociation at 193 nm

(Diatomics understood)



## <u>HBr $\rightarrow$ H + **Br** (J=1/2)</u>

RR



 $\frac{I_{RCP}}{I_{LCP}} = 2.0 \pm 0.2$ 

RL





## <u>HBr $\rightarrow$ H + **Br** (J=3/2)</u>

RR



 $\frac{I_{RCP}}{I_{LCP}} = 1.6 \pm 0.2$ 

RL





HBr Photodissociation at 193nm Rakitzis et al., JCP, 121, 7222 (2004).



## Results (along photolysis polarization)



Unsatisfying that H-atom detection is not direct...

## Can the SPH be seen directly?



Selection Rules (one-photon dipole transition)  $\Delta m=0$  and  $\Delta m=\pm 1$  NOT with same axis (linearly p.l.) (circularly p.l.)



## SPH fluorescence detection



T.P. Rakitzis, *ChemPhysChem*, **5**, 1489 (2004).

Advantages:

ges: 1) Hyperfine resolution not necessary
2) Sensitive to SPH velocity (Doppler shift)
3) Detect on nanosecond timescale
4) Very sensitive

## **Experimental Setup**



#### VUV $\lambda/4$ plate



VUV polarizer Interaction region







Theory: Brown & co., JPC.A., 108 (2004) 7790; 110 (2006) 5371.

## SPH production at BNL (current density record)







## SPH production and detection on Crete





## "Single-molecule Stern-Gerlach Spin-Separator"



Only recently we extended this work to production of spin-polarized D (SPD):

#### I(<sup>2</sup>P<sub>3/2</sub>) polarization from DI photodissociation at 270 nm



Linearly polarized geometries

#### I(<sup>2</sup>P<sub>3/2</sub>) polarization from DI photodissociation at 270 nm



• D atoms highly electron spin polarized (~100%)

#### Theory for D and H polarization from DI and HCI photodissociation



Alex Brown et al.

J. Chem. Phys. 122, 084301 (2005)

J. Phys. Chem. A 2004, 108, 7790

#### I(<sup>2</sup>P<sub>3/2</sub>) and D(<sup>2</sup>S<sub>1/2</sub>) polarized OPPOSITELY



D nucleus polarized 60% after 1.6 ns (hyperfine beating)

Photolysis laser pulse should be < 1 ns



100% polarized H<sup>+</sup> or T<sup>+</sup>, and 60% polarized D<sup>+</sup> can be produced, if:

1) Photodissociation of hydrogen halide happens at correct wavelength, where electron polarization is 100%.

2) Bond of hydrogen halide is aligned parallel to laser polarization, or only those recoiling atoms are selected

3) Timing between photodissociation and ionization lasers allows 100% transfer of polarization from electron to nuclear spin (half the hyperfine beating period). <u>Pump-probe polarized Fusion</u> (D-D, and D-<sup>3</sup>He or D-T)



#### **National Ignition Facility (NIF, Livermore CA**



#### Measurement of O<sub>2</sub> electron spin polarization at 2.7 x 10<sup>19</sup> cm<sup>-3</sup>



V. Milner "Ultrafast magnetization of a dense molecular gas with an optical centrifuge" PRL (2017)

## **Conclusions II**

1) Spin-polarized H/D/T can be produced from hydrogen halide photodissociation.

2) More work is needed for H/D/T halides (F, Cl, Br, I) and at different laser wavelengths (157-300 nm), to see when polarization is maximal (hopefully near 100%).

### Conclusions

- Spin-polarized H/D/T can be produced using two methods using molecules:
- 1) UV photodissociation

Perhaps both methods can be combined

(high densities, production rates)

2) IR rovibrational excitation

(high production rates, high D polarization, high  $P_{zz}$  polarization)

• Appropriate lasers in the UV and IR exist with  $>10^{22}$  photons/s;

Can ionization methods keep up?

• These methods should be considered for many applications in spin physics, including those discussed here!

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