

QUANTUM-STATE DETECTION OF MOLECULAR HYDROGEN IN GAS-GAS AND GAS-SURFACE  
SCATTERING EXPERIMENTS

Greg. O. SITZ, Richard S. BLAKE, Thomas A. STEPHENSON, and Richard N. ZARE  
Department of Chemistry, Stanford University, Stanford, California 94305  
Glenn D. KUBIAK

Sandia National Laboratories, Livermore, California 94550

ABSTRACT: We have used the technique of resonance-enhanced multiphoton ionization to detect molecular hydrogen in a quantum state specific manner. We report on the use of this technique to determine accurate ro-vibrational state populations in scattering experiments where  $H_2$ , or its isotopic variations, are products.

RESUME : Nous avons utilisé la technique d'ionisation résonnante à plusieurs photons pour réaliser une détection sélective en état interne de l'hydrogène moléculaire. Nous décrivons les populations rovibrationnelles ainsi déterminées dans des expériences de collision produisant la molécule de  $H_2$  ou une de ses variantes isotopiques.

## I. INTRODUCTION

The hydrogen molecule is of widespread theoretical and practical importance. In the past, the majority of studies of the dynamics of processes involving hydrogen have focused on the distributions of the center-of-mass variables such as angle and velocity. This is due to the fact that hydrogen has been very difficult to detect in an internal state resolved manner due to the lack of low lying excited electronic states which could be accessed with convenient light sources. Recently, however, several schemes have been developed to detect hydrogen in a quantum-state specific manner at low densities. Marinero, Rettner, and Zare have employed 2+1 resonance-enhanced multiphoton ionization (REMPI) through the E,F state (1). Several groups have described the use of tunable VUV light to excite hydrogen: Rottke and Welge have reported 1+1 REMPI through the B state (2); Northrup et al. (3) have demonstrated single photon laser induced fluorescence (LIF) to the B state; Kung et al. (4) have explored both 1+1 REMPI and LIF to the B and C states. Gerrity and Valentini (5) have shown the applicability of CARS. Here we examine further the use of 2+1 REMPI through the E,F state as a technique of detecting molecular hydrogen in a scattering experiment, and describe the reduction of measured line intensities to yield accurate, quantum state populations. We use as examples two experiments conducted in our laboratory, namely 1) the gas phase reaction  $H + D_2 \rightarrow HD + H$  (6) and 2) the recombinative desorption of  $H_2$  ( $D_2$ ) from Cu(111) and Cu(110) surfaces (7,8).

Experimental studies of the dynamics of the reaction  $H + D_2 \rightarrow HD + H$  permit a detailed comparison to be made with accurate ab-initio calculations of the potential energy surface.  $H_3$  is the simplest reactive system and has been extensively studied theoretically, so experimental results may offer a stringent test of modern quantum chemistry.

In the recombinative desorption of hydrogen from copper, the well known barrier for dissociative adsorption (9) is known to give rise to interesting dynamics in desorption. The average translational energy of  $D_2$  recombinatively desorbing from Cu was found to be almost twice the equilibrium value (10), and the angular distributions were found to be strongly peaked along the surface normal (11). Thus, measurements of the internal state distributions are expected to strongly reflect the details of the potential energy surface governing the reaction.

