

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

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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.

II. EXPERIMENTAL

The apparatus used in these studies have been described in detail elsewhere (6,7;8) so only a brief summary will be given here. This summary will be divided into two parts: part 1) describes the scattering chambers used in the two experiments and 2) describes the laser system used to generate the light to excite the 2 photon transition and subsequent ionization $H_2^+ X^2\Sigma_g^+ + H_2 E, F^1\Sigma_g^+ + X^1\Sigma_g^+$.

1) Scattering Chambers

A diagram of the apparatus used for the gas phase $H + D_2$ reactions is shown in Fig. 1, a complete description of which is given in Ref. 6. Hot H atoms are generated by photolysis of HI at 266 nm, yielding a center-of-mass collision energy of 1.3 eV. After a suitable delay to allow the

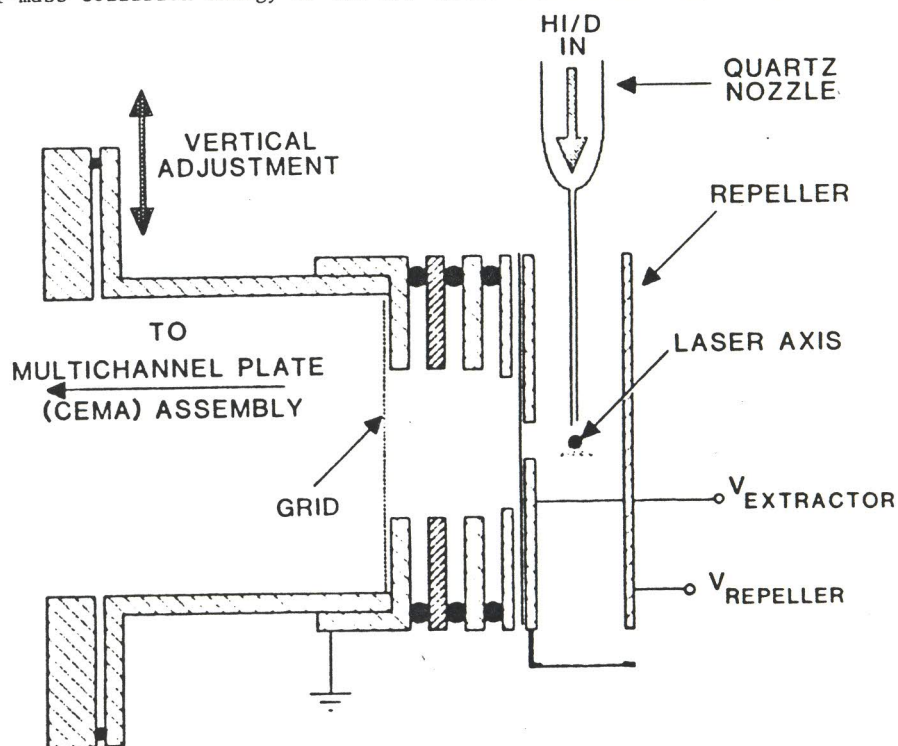


Figure 1. Detailed drawing of the apparatus used in the study of the $H + D_2$ reaction showing the reaction zone and ion extraction plates. The glass delivery tube is also shown.

reaction to occur, the HD reaction product is ionized by the technique described in part 2) below, and detected in a time-of-flight mass spectrometer (TOF-MS). The photolysis laser and the probe laser are counterpropagating and colinear. The cross sectional area of the photolysis laser is ~ 5 times that of the probe laser to minimize problems associated with product "fly-out" from the reaction zone. The total density in the reaction region is about 1×10^{-4} torr.

In the surface experiment, hydrogen is supplied to the surface as atoms by permeation through the bulk of a copper single crystal from a high pressure region. Figure 2 shows a schematic drawing of the setup (7,8). The surface temperature is typically 850-950 K. The atoms recombine on the surface and desorb into the vacuum. The density just

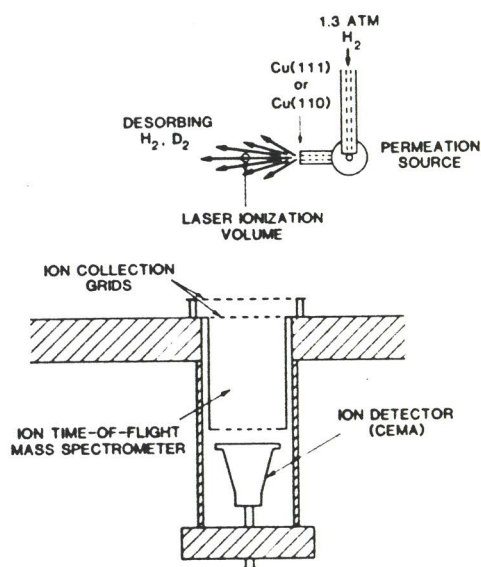


Figure 2. Schematic drawing of the apparatus used in the study of the recombinative desorption of hydrogen from copper surfaces.

above the surface is estimated to be 1.6×10^9 molecules/cm³. The desorption flux is crossed with a focused laser beam, and the resulting ions are detected, as in the gas phase reaction, with a TOF-MS. The vacuum chamber is equipped with Low Energy Electron Diffraction (LEED) and Auger

Electron Spectroscopy (AES) for verifying surface geometric order and chemical composition respectively. The surface is periodically cleaned by argon ion sputtering.

2) Laser Excitation Scheme

Tunable radiation in the range 190-210 nm is generated as follows. The output of a ND3+:YAG pumped dye laser (operating in the range 560-600 nm) is frequency-doubled and focused into a Raman cell containing 3-5 atm of H₂. Stimulated Raman scattering occurs and generates light differing in energy from the fundamental by integral multiples of the H₂ Q1 $v''=1 + v''=0$ transition energy (4155 cm⁻¹). Anti-Stokes (AS) orders gain 1 or more quanta, and Stokes orders similarly lose energy. Conversion efficiency into the higher AS orders is found to be critically dependent on the combination of cell pressure and focussing conditions (and even on the relative position of the focussing lens and laser beam axes)(12).

In the surface experiment, the undispersed output of the Raman cell is directed into the chamber and focused into the desorption flux. The 3rd AS and 4th AS (at 211 nm and 194 nm respectively for a dye laser wavelength of 571 nm) excite the (0,0) band of the H₂ E,F + X transition. In addition, two 3rd AS photons excite the (1,0) band, so data for both vibrational levels can be collected in a single scan. The high power density from the residual doubled dye and lower AS orders insure that all the hydrogen excited to the E,F state is effectively ionized. Figure 3 shows this excitation scheme and the relevant H₂ potential curves. A small fraction of the incident laser beam is split off, dispersed, and the intensity of the 3rd and 4th AS orders are monitored during a scan.

In the gas phase experiment, the 4th AS order is separated from the other wavelengths present and focused into the reaction region. It is necessary to disperse the output of the Raman cell in this case because the residual light in the undispersed beam dissociates and nonresonantly ionizes the HI present, nearly overloading the ion detector. However, the power in the single AS order is often insufficient to saturate the ionization step. To solve this problem, the residual IR from the ND3+:YAG is frequently tripled, suitably delayed, and focused at the same spot as the excitation light, thus assuring 100% ionization of the excited H₂.

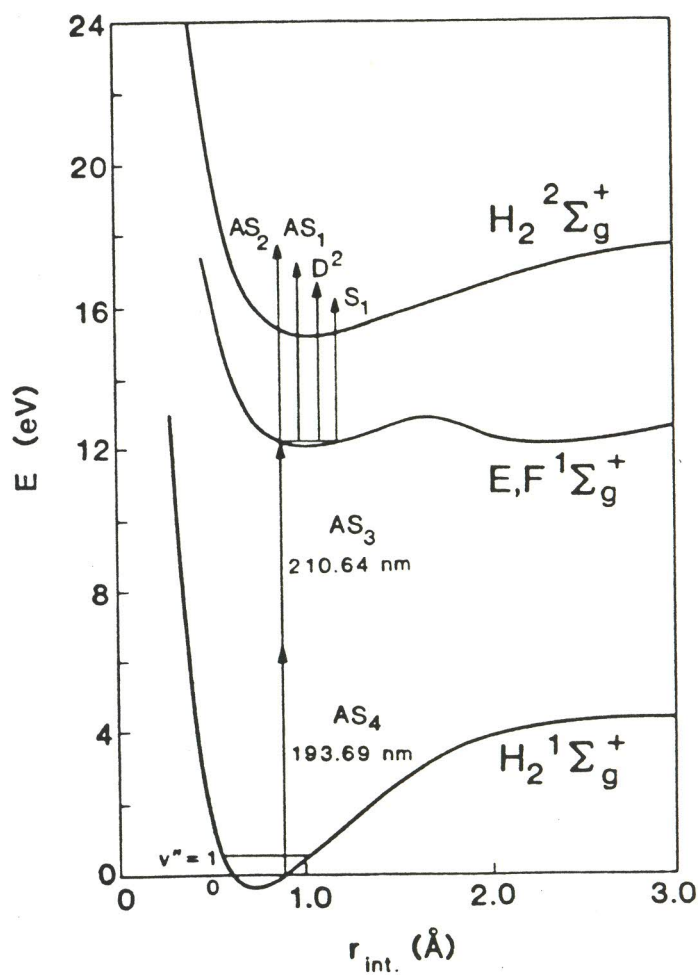


Figure 3. Diagram of the 2+1, resonance-enhanced multiphoton ionization technique to detect molecular hydrogen.

III. RESULTS AND DISCUSSION

Figure 4 shows a typical spectrum, in this case of H_2 recombinationally desorbing from Cu(111). In general the use of REMPI to determine relative quantum state populations requires an independent calibration standard. This is so because excitation cross sections may not be well known (as they generally are in a 1 photon process), and also the ionization efficiency may vary in a poorly defined manner with v and J . When the

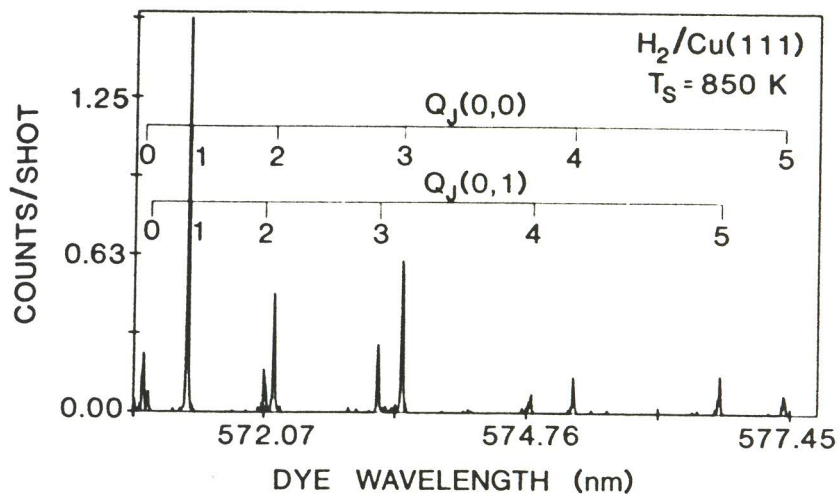


Figure 4. Resonance-enhanced multiphoton ionization spectrum of H_2 desorbing from Cu(111) at $T_s = 850$ K.

ionization probability out of the intermediate level has no quantum state or laser intensity dependence (i.e. is saturated), then the population of a given rotational state within a vibrational band, $P(v'', J'')$, would be related to the spectral line intensity $I(v'', J'')$ by an expression such as

$$P(v'', J'') = I(v'', J'') / \{S(J', J'')g(J'', n)I(AS(n))I(AS(n'))\} \quad (1)$$

where $S(J', J'')$ is the two photon line strength, $g(J'', n)$ is the degeneracy of the state (including both rotational and nuclear spin degeneracies), and $I(AS(n))I(AS(n'))$ is the product of the intensities of the two Anti-Stokes orders used to excite the $E, F + X$ transition. The two photon line strengths have been calculated by Bray and Hochstrasser (13) and, since they are all very close to unity for the Q branch of a $\Sigma + \Sigma$ transition, they have been neglected (12). Figure 5 shows a plot of $\ln(I(v, J))$ vs. $\ln I(AS4)$ for a background sample of $HD(v''=0)$. The slope is very nearly 2 indicating the assumptions made in Eq. 1 are valid for this branch. To provide a reference source we have utilized a free jet source, constructed of tungsten, which can be heated to temperatures, T_0 , in excess of 2100 K. This source is uniformly heated over ~ 5 cm of its length to ensure that the gas is fully equilibrated at the source temperature.

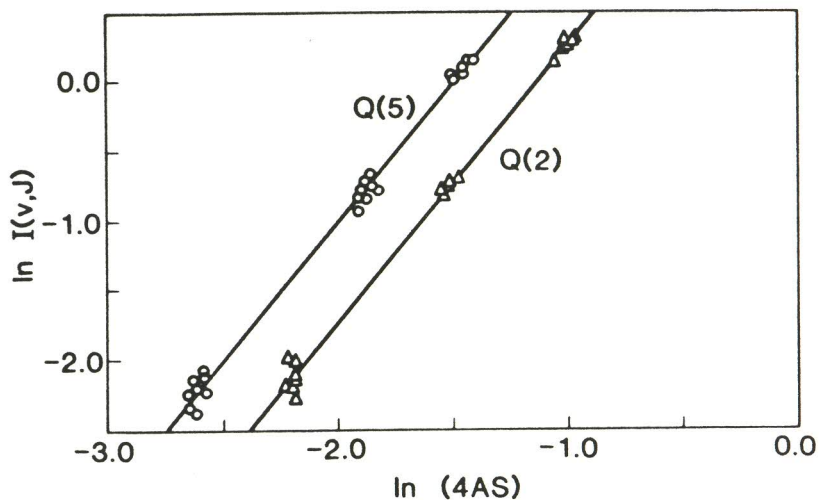


Figure 5. Plot of $\ln(I(J))$ vs $\ln(4AS)$ for various Q branch members of the (0,0) band of HD. The slopes of the lines plotted are both $2.00 \pm .05$.

Rotational relaxation of hydrogen in supersonic molecular beam expansions has been studied by Gallagher and Fenn (14) using time-of-flight techniques. From their results and our relatively mild expansion conditions ($P = 1$ atm, $d = 25 \mu\text{m}$) we estimate a final rotational temperature T_r , of $0.9 T_o$. Figure 6 is a REMPI spectra of jet expanded H_2 for a source temperature of 1700 K. The rotational distributions are determined from such spectra using Eq. 1 and are found to be well characterized by a temperature, i.e. the distributions are Boltzmann. Table 1 lists the source conditions used, and the temperatures corresponding to the best fit lines. Note that our measured temperatures are systematically 10-20% lower than the source temperature, in good agreement with the results of Gallagher and Fenn. Moreover, spectra of room temperature (22°C) static gas samples yield rotational temperatures of 295 ± 3 K. It is clear from these results that the determination of rotational distributions is well in hand.

The ionization probability using REMPI varies strongly with v'' . Therefore to determine vibrational populations, the observed variation in

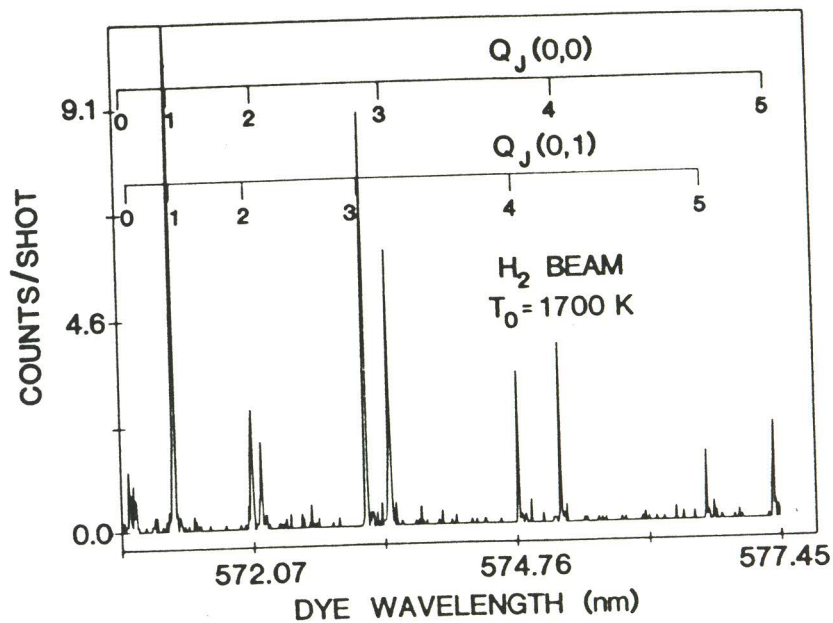


Figure 6. Resonance-enhanced multiphoton ionization spectrum of H_2 in a heated free jet source at a stagnation pressure of 1 atm and temperature of 1700 K.

ionization probability must be calibrated. The nozzle beam can also be used as a source of well defined vibrational populations. Vibrational relaxation in hydrogen expansions is expected to be slow, although the possibility of near-resonant vibration to rotation energy transfer has been suggested for H_2 (14), so we have adopted the relatively safe assumption of Gallagher and Fenn that $T_v = T_r$.

T_0 (K)	1224	1352	1465	1575	1693	2015	$\langle T_r/T_0 \rangle$
$H_2(v''=0)$	961	1209	1326	1445	1621	2430	0.94 ± 0.15
T_r (K)							

Table 1. Values of T_r as a function of T_0 for H_2 .

1) Gas Phase H + D₂

A complete discussion of the results of this experiment can be found in Ref. 6. Current efforts are aimed at increasing the accuracy of previous measurements, extending the analysis to the product v''=0 level, and performing the experiment at other center-of-mass collision energies.

2) Recombinative Desorption

From comparison of the reaction spectrum of Fig. 4 and the reference spectrum of Fig. 6 one qualitative conclusion can immediately be drawn regarding the vibrational distribution in desorption, namely that it is hot. The relative v''=1 signal in Fig. 4 for a surface temperature of 850 K is close to that observed in the 1700 K beam spectrum of Fig. 6. On Cu(110) the vibrational population ratio P(v''=1)/P(v''=0) was found to be ~50 times that characterizing an equilibrium distribution at the surface temperature. On Cu(111) the ratio was ~100. A full presentation of the data and a discussion of possible mechanisms to account for the vibrational excitation observed has been given elsewhere (7,8).

In contrast to the vibrational distributions, the rotational distributions were found to be non-Boltzmann and to yield mean rotational energies slightly (10-20%) less than the surface temperature. The rotational distributions were found to be the same for desorption from both Cu(111) and Cu(110). The (111) surface is microscopically flat, whereas the (110) surface is very corrugated. Thus the rotational distributions indicate that recombination is occurring in a region where modulation of the atom/molecule-surface potential due to surface structure is weak. A complete discussion of the rotational distributions is also given in Ref. 8.

The weakest transition observed in the spectrum shown in Fig. 4 is the Q4 line of the (1,0) band. Our results (8) indicate that this state accounts for about 0.7% of the total desorption flux. Thus the estimated density in this state is approximately 1.0×10^6 molecules/cm³ indicating good sensitivity at low densities.

IV. CONCLUSION

In the preceding sections, some examples have been presented to illustrate the use of 2+1 REMPI to study the dynamics of simple reactions which yield H₂ of its isotopic analogs as products. The detailed infor-

mation gained from these studies, coupled with more accurate calculations promise to significantly extend our knowledge of basic reaction dynamics.

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REFERENCES

1. a. E. E. Marinero, C. T. Rettner, and R. N. Zare, *Phys. Rev. Lett.* 48, 1323 (1982).
b. E. E. Marinero, R. Vasudev, and R. N. Zare, *J. Chem. Phys.* 78, 692 (1983).
2. H. Rottke and K. H. Welge, *Chem. Phys. Lett.* 99, 456 (1983).
3. F. J. Northrup, J. C. Polanyi, S. C. Wallace, and J. M. Williamson, *Chem. Phys. Lett.* 105, 34 (1984).
4. A. H. Kung, N. A. Gershenfeld, C. T. Rettner, D. S. Bethune, E. E. Marinero, and R. N. Zare, in "Laser Techniques in the Extreme Ultraviolet," AIP conference proceedings, edited by S. E. Harris and T. B. Lucetoro (1984).
5. D. P. Gerrity and J. J. Valentini, *J. Chem. Phys.* 79, 5202 (1983).
6. E. E. Marinero, C. T. Rettner, and R. N. Zare, *J. Chem. Phys.* 80, 4142 (1984).
7. G. D. Kubiak, G. O. Sitz, and R. N. Zare, *J. Chem. Phys.* 80, 6397 (1984).
8. a. G. D. Kubiak, G. O. Sitz, and R. N. Zare, *J. Vac. Sci. Tech.* in press.
b. G. D. Kubiak, G. O. Sitz, and R. N. Zare, *J. Chem. Phys.* in press.
9. M. Balooch, M. J. Cardillo, D. R. Miller, and R. E. Stickney, *Surface Sci.* 46, 358 (1974).
10. G. Comsa and R. David, *Surface Sci.* 117, 77 (1982).
11. M. Balooch and R. E. Stickney, *Surface Sci.* 38, 313 (1973).
12. G. D. Kubiak, Ph.D. thesis, Stanford University, unpublished.
13. R. G. Bray and R. M. Hochstrasser, *Mol. Phys.* 31, 1199 (1975).
14. R. J. Gallagher and J. B. Fenn, *J. Chem. Phys.* 60, 3492 (1974).