

Lawrence Berkeley National Laboratory

Recent Work

Title

Ultrasensitive Detection of Hydrogen Molecules by (2+1) [REMPI] Ultrasensitive Detection of Hydrogen Molecules by (2+1) REMPI{Resonance-Enhanced Multiphoton Ionization]

Permalink

<https://escholarship.org/uc/item/2zk9g8mx>

Journal

Review of Scientific Instruments, 64(3)

Authors

Vrakking, M.J.J.

Bracker, A.S.

Suzuki, T.

et al.

Publication Date

1992-09-01

LBL-32881
UC-401
Preprint



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

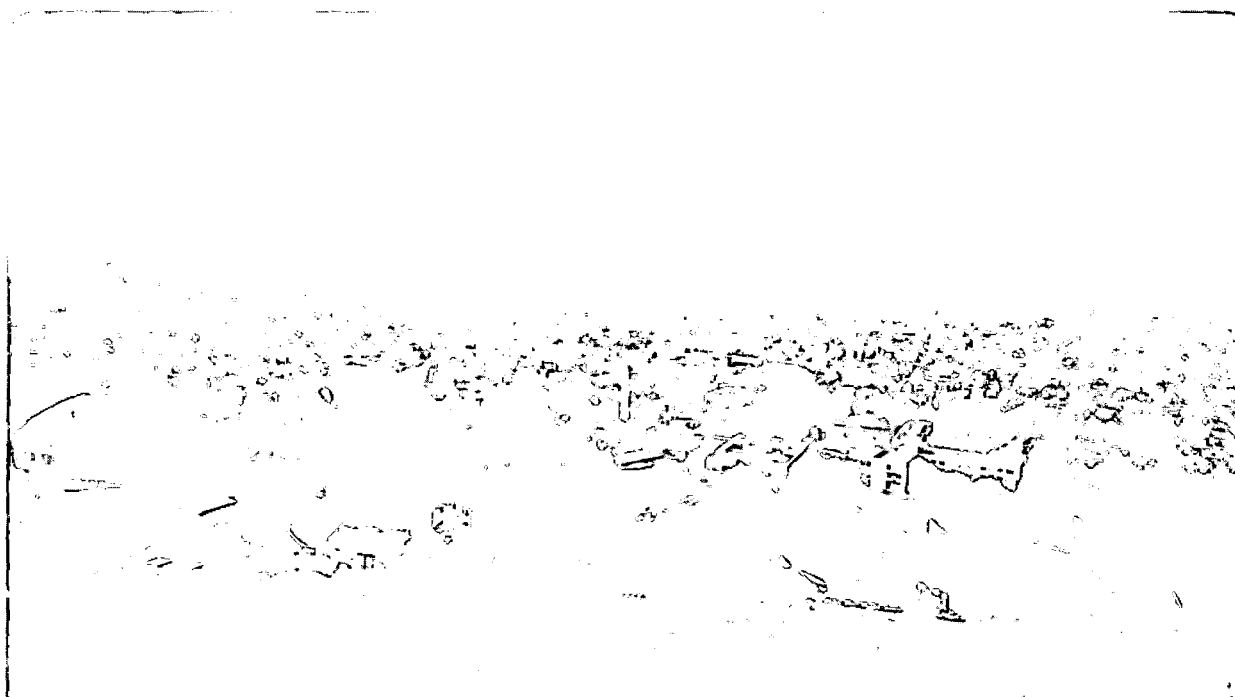
CHEMICAL SCIENCES DIVISION

Submitted to Review of Scientific Instruments

Ultra-Sensitive Detection of Hydrogen Molecules by (2+1) REMPI

M.J.J. Vrakking, A.S. Bracker, T. Suzuki, and Y.T. Lee

September 1992



LOAN COPY |
Circulates |
for 4 weeks |
Bldg. 50 Library.
Copy 2

LBL-32881

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. Neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or The Regents of the University of California and shall not be used for advertising or product endorsement purposes.

Lawrence Berkeley Laboratory is an equal opportunity employer.

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

ULTRA-SENSITIVE DETECTION OF HYDROGEN MOLECULES BY (2+1) REMPI

Marcus J.J. Vrakking, Allan S. Bracker,
Toshinori Suzuki and Yuan T. Lee

*Chemical Sciences Division, Lawrence Berkeley Laboratory,
and Department of Chemistry, University of California at Berkeley,
Berkeley, California 94720, USA*

September 1992

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

ULTRA-SENSITIVE DETECTION OF HYDROGEN MOLECULES BY (2+1) REMPI

Marcus J.J. Vrakking, Allan S. Bracker^{a)},
Toshinori Suzuki^{b)} and Yuan T. Lee

*Chemical Sciences Division, Lawrence Berkeley Laboratory,
and Department of Chemistry, University of California at Berkeley,
Berkeley, California 94720, USA*

September 1992

ABSTRACT

Ultra-sensitive detection of molecular hydrogen is reported by using Doppler-free (2+1) REMPI through the E,F $1\Sigma_g^+$ state. By using an arrangement with two near transform-limited counterpropagating laser beams, a *single shot* detection efficiency of $6.8 \cdot 10^3$ molecules/cm³ has been demonstrated. Frequency scans of the two-photon transitions show that the detection efficiency is limited by AC Stark effects.

a) NSF Predoctoral Fellow.

b) Current address: Institute for Molecular Science, Myodaiji, Okazaki, Japan.

I. Introduction

Over the last ten years laser-based detection schemes have enabled physical chemists to study in ever greater detail the dynamics of chemical reactions and photodissociation processes. Techniques such as Coherent Anti-Stokes Raman Scattering (CARS), Laser-Induced Fluorescence (LIF), degenerate four-wave mixing and Resonance-Enhanced Multi-Photon Ionization (REMPI) are the more common laser schemes in use today, with the latter clearly being the most sensitive technique.

State-specific detection of the hydrogen molecule has been of particular interest. There are a large number of studies which have explored the ro-vibrational product state distributions of the hydrogen molecule formed by photodissociation and from the reaction $D/H + H_2 \rightarrow DH/H_2 + H$. State-specific detection of the molecular products of this reaction was carried out previously by Valentini and co-workers using CARS, and by Zare and co-workers using REMPI¹⁾. The goal in both of these experiments was the determination of the final product state distributions. Our primary interest is in the (angle-resolved) differential cross-sections for specific final ro-vibrational states, which can be accessed by application of a crossed molecular beam technique²⁾. These difficult experiments are possible provided that the detection efficiency for the hydrogen molecule can be improved with respect to the values that have been reported previously in the literature, namely approximately $1.7 \cdot 10^5$ molecules/cc using (1+1) xuv+uv REMPI through the B- and C- state³⁾, and approximately 10^6 molecules/cc for a (2+1) REMPI scheme through the E,F- state⁴⁾. In the current paper we demonstrate a *single shot* detection efficiency of approximately $6.8 \cdot 10^3$ molecules/cc by using a Doppler-free (2+1) REMPI scheme where the key is the use of two near-transform limited counterpropagating laser beams.

The use of Doppler-free two-photon resonant excitation schemes is a very popular technique in high-resolution spectroscopy⁵⁾, and a series of impressive results have been obtained with this method⁶⁾. However, with a few exceptions⁷⁾, the use of a Doppler-free two-photon technique with the aim of achieving superior detection efficiencies has hardly been explored. In studies of chemical reaction dynamics the molecules to be detected frequently travel over a wide range of laboratory velocities and angles, leading to an effective Doppler width which can significantly exceed the bandwidth of the lasers used for the detection. In our $D + H_2$ experiment,

for example, the effective Doppler width for a typical ro-vibrational product state is approximately 3 cm^{-1} . It is in these situations in particular, that application of a Doppler-free two-photon technique may be the preferred way to probe the number density of a particular ro-vibrational product state in a given volume element.

Two-photon excitation of H_2 to the E,F $^1\Sigma_g^+$ state was first demonstrated by Kligler and Rhodes⁸. The first rotational analysis for this transition was published by Marinero et.al.⁹ and later refined by Eyer et.al.¹⁰. For all isotopic combinations, detailed comparisons between the ab-initio transition moments and the relative experimental (2+1) REMPI probabilities were published in a series of papers by Zare et.al.^{4,11}. A number of groups have used two-photon excitation of H_2 to the E,F $^1\Sigma_g^+$ state as a starting point for studies of H_2 Rydberg states^{12,13}.

The organization of this paper is as follows. In Section II, a theoretical comparison between (1+1) REMPI and (2+1) REMPI of the hydrogen molecule will be presented, illustrating the relative merits of both techniques in particular situations. In Section III, the experimental arrangement will be described and in Section IV results for the detection of trace amounts of DH will be presented.

II. Theory

a) (1+1) REMPI and (2+1) REMPI

Following from first order perturbation theory, the fraction of molecules that will undergo a one-photon transition from initial state $|g\rangle$ to final state $|k\rangle$ is given as¹⁴⁾

$$\frac{N_k(t)}{N_g(t)} = \frac{32\pi^3 q^2 A_0^2 t}{h^2} |\tilde{e} \cdot \langle g | \vec{r} | k \rangle|^2 \int_0^\infty g_M(\omega_{av}) g_L(\omega_{av}) \omega_{av}^2 d\omega_{av} \quad (1)$$

where $g_M(\omega)$ and $g_L(\omega)$ are the molecular and the laser frequency distribution, respectively, which are both normalized to unity. This equation shows that two situations can occur depending on the relative widths of the frequency distributions of the laser and the molecule. If the molecular linewidth is much narrower than the laser linewidth, then $g_M(\omega)$ will be a much sharper function than $g_L(\omega)$, and consequently the integral can be approximated by $\omega^2 g_L(\omega)$, indicating that the laser linewidth, rather than the molecular linewidth, puts a limit on the upumping rate. On the other hand, if the laser linewidth is much narrower than the molecular linewidth, the integral can be approximated by $\omega^2 g_M(\omega)$, and apart from the photonflux of the laser [photons/cm²],

$$F = \frac{\pi \omega A_0^2}{\mu_0 h c} \quad (2)$$

the upumping rate is uniquely determined by the absorption cross section of the molecule, which can be written as

$$\sigma_{gk} = 64\pi^2 \alpha \omega g_M(\omega) |\langle g | \vec{r} | k \rangle|^2 \quad (3)$$

where α is the fine-structure constant.

The occurrence of two-photon absorptions follows from second order perturbation theory. The two-photon transition rate is found to be

$$\begin{aligned}
 W_{gf}^{(2)} &= \frac{1}{N_g} \left(\frac{d}{dt} \right) N_f \\
 &= 128\pi^5 \frac{q^4 A_0^4}{h^4} \iint |S_{gf}|^2 \omega_{av}^4 g_M(2\omega_{av}) g_L(\omega_{av}) d\omega_{av}
 \end{aligned} \tag{4}$$

A dependence on the linewidth of the laser and the linewidth of the molecular transition similar to the one-photon case, can be recognized. Rewriting Equation [4] in terms of the laser power I [W/cm²], and performing the integral over ω_{av} leads to the following convenient equations for the two-photon absorption cross section and the effective two-photon absorption rate:

$$\begin{aligned}
 \sigma_{gf}^{(2)} &= \alpha I \\
 &= \frac{(2\pi)^4}{hc^2} \omega |M_{gf}|^2 g_{effective}(\omega) I
 \end{aligned} \tag{5}$$

and

$$\begin{aligned}
 W_{gf}^{(2)} &= \sigma \frac{2\pi I}{h\omega} \\
 &= \frac{(2\pi)^5}{h^2 c^2} |M_{gf}|^2 g_{effective}(\omega) I^2
 \end{aligned} \tag{6}$$

where the two-photon transition moment M_{gf} has been introduced as

$$|M_{gf}|^2 = \left| \sum_k \frac{(\vec{e} \cdot \langle g | \vec{\mu} | k \rangle) (\langle k | \vec{\mu} | f \rangle \cdot \vec{e})}{E_{kg} - \frac{h\omega}{2\pi}} \right|^2 \tag{7}$$

and the integral over the lineshape distributions has been replaced by an effective lineshape $g_{\text{effective}}(\omega)$. Unlike the one-photon case, the two-photon absorption cross section is proportional to the laser power, in agreement with the fact that the two-photon absorption rate has a quadratic dependence on laser power.

The application of a (2+1) REMPI technique opens up the possibility of setting up a counterpropagating laser arrangement in which the Doppler shifts with respect to the two laser directions cancel and the first order Doppler shift drops out of the resonance condition:

$$\omega_{gf} = \omega \left\{ \left[1 + \frac{u_x}{c} \right]_{\text{laser I}} + \left[1 - \frac{u_x}{c} \right]_{\text{laser II}} \right\} = 2\omega \quad (8)$$

Thus, in the absence of additional line broadening mechanisms, the molecular linewidth $g_M(\omega)$ reduces from the Doppler width to the natural linewidth, and when the laser frequency is tuned to satisfy the resonance condition, all molecules will be able to absorb two photons, one from each laser beam, independent of their velocity vector. The lifetimes of the states that are accessed in the two-photon process are about 100 nsec¹⁵, and thus the natural linewidth is considerably narrower than the linewidths which are achievable in most high power pulsed laser systems. Therefore, if there are no other line broadening mechanisms, the effective linewidth function $g_{\text{effective}}(\omega)$ in Equations [5] and [6] becomes equivalent to the laser linewidth function $g_L(\omega)$, and it will prove advantageous to use a narrowband laser in this detection scheme. This should come as no surprise, since the probability of finding a 'matching photon' in the second, counterpropagating laser is inversely proportional to the bandwidth of the laser.

b) Comparison of the detection efficiencies for molecular hydrogen using (1+1) REMPI and (2+1) REMPI

The most precise quantitative work on the efficiency of hydrogen detection by (1+1) xuv+uv REMPI through the B- or C-state was published a few years ago by Kung et.al.³⁾ Using frequency-tripling of the doubled output of a 0.3 cm⁻¹ linewidth pulsed dye laser, these authors

report a noise-limited detection limit of $1.7 \cdot 10^5$ H₂ molecules/cc in a given quantum state over an integration period of 100 lasershots, corresponding to a *single shot* detection limit of $1.7 \cdot 10^6$ molecules/cc. In this experiment, the laser linewidth was 0.8 cm^{-1} (24 GHz) at the extreme ultraviolet (xuv) transition frequency, which is much larger than the molecular linewidth, which is a combination of the natural linewidth (approximately 250 MHz) and the residual Dopplerwidth of the molecular beam used. Thus it follows from Equation [1] that it is possible to increase the excitation rate (and thus the detection sensitivity) by nearly two orders of magnitude when the relatively broad bandwidth laser of Kung et.al. is replaced by a more narrowband xuv laser. In fact, Cromwell reports a detection efficiency of $\approx 10^4$ molecules/cc for molecules with a Dopplershift within the bandwidth of a near transform-limited 210 MHz FWHM xuv laser¹⁶⁾.

However, here a major problem with the (1+1) technique is encountered. The high detection sensitivity achieved with the near-transform limited laser is only available as long as the molecular linewidth is smaller than or roughly equal to the laser linewidth. If there is a mechanism that broadens the molecular linewidth beyond the laser linewidth, Equation [1] shows that the narrow linewidth of the laser ceases to benefit the detection efficiency, which instead becomes inversely proportional to the linewidth of the molecular transition. In the experiments on the hydrogen exchange reaction which we carry out in our laboratory, the typical effective Doppler width of the hydrogen product molecules is about 3 cm^{-1} . Using the higher value for the detection efficiency reported by Cromwell it follows that in this case the detection sensitivity would drop to about $4.3 \cdot 10^6$ molecules/cc for the (1+1) REMPI technique. It should be pointed out that the hydrogen exchange reaction is by no means an exceptional case. In many situations of chemical interest, large effective Doppler widths are encountered, where the detection efficiency using (1+1) REMPI will drop to 10^6 - 10^7 molecules/cc.

In order to calculate the efficiency of the two-photon process, Equation [6] describing the rate of the two-photon absorption is brought into the following form:

$$W_{gf}^{(2)} [\text{sec}^{-1}] = 1.2 \cdot 10^{-9} * |M_{gf}|^2 [\text{a.u.}] * I_{laser}^2 \left[\frac{W^2}{\text{cm}^4} \right] \quad (9)$$

where it has been assumed that a counterpropagating laser beam arrangement exists with two beams of equal laser power I_{laser} . Furthermore, reflecting conditions existing in our experiment, a 150 MHz laser bandwidth was used to obtain Equation [9]. The transition moments for the hydrogen two-photon excitations used in this scheme have been determined in an ab-initio quantum mechanical calculation and have been compared experimentally with results obtained for known ro-vibrational state populations. For DH Q-branch excitations $E, F \ ^1\Sigma_g^+(v'=0, J'=J'') \leftarrow X \ ^1\Sigma_g^+(v''=0, J')$, the squared transition moments are found to be approximately 7 atomic units, whereas for excitations DH E, F $\ ^1\Sigma_g^+(v'=1, J'=J'') \leftarrow X \ ^1\Sigma_g^+(v''=1, J'')$, the squared transition moments are approximately 24 atomic units⁴). Although not constant, the transition moments are relatively insensitive to the choice of the rotational quantum number.

The application of (2+1) REMPI detection requires the generation of laser light around 200 nm. As discussed in the next section, it is possible to generate several mJ/pulse at these wavelengths. An estimate of the upumping rate can be obtained by assuming a power of about 0.5 mJ/pulse for both counterpropagating laser beams and an experimental 201 nm pulse length of about 7 nsec. If the laser beams are focussed to a waist of 300 μm , then the laser power will be 10^8 W/cm^2 and the two-photon upumping rate for $\text{H}_2(v''=0)$ is found to be about $8.4 \cdot 10^7 \text{ sec}^{-1}$. The significance of this result can be understood if the rate equation for depopulation of the ground state is considered. Assuming a typical photoionization cross section of 10^{-17} cm^2 , the rate of the single-photon ionization step is about 10^9 sec^{-1} at the laser power given above, and therefore it will be assumed that after the initial excitation the molecule is immediately ionized and there are no two-photon transitions from the excited state to the ground state. The depopulation of the ground state is then given by

$$\frac{dN_g}{dt} = -W_{gE}^{(2)} N_g \quad (10)$$

so after the laser pulse is over

$$\begin{aligned} N_g &= N_{g,0} \exp [-W_{gf}^{(2)} \Delta T_{laser}] \\ N_{ion}^+ &= N_{g,0} (1 - \exp [-W_{gf}^{(2)} \Delta T_{laser}]) \end{aligned} \quad (11)$$

and we find that in this situation about 45 % of the molecules which were initially in the ground state are ionized.

The calculation given above can be related to the detection efficiency. Similar to the case of (1+1) REMPI, it will be assumed that the detection limit for the experiment lies at the point where in a *single* lasershot a signal-to-noise ratio of unity can be achieved. This means that in a background-free experiment we need to detect on average one ion per lasershot. In the current experiment, detection of ions is possible over a length of 2.5 cm along the laseraxis. This means that when the laser is focussed to a 300 μm spot, as described above, the size of the effective detection volume will be 1.8 mm^3 . Using the result of the calculation that on average 2.3 DH molecules are required in the detection volume in order to detect a single ion, this would lead to a detection sensitivity of approximately 1300 molecules/ cm^3 , which, in addition to the fact that it *does not* require the molecules to have a particular Doppler shift, is almost one order of magnitude better than the (1+1) REMPI detection efficiency reported by Cromwell.

The calculated dependence of the ion signal on the size of the detection volume is shown in Figure 1 for two values of the laser power in both counterpropagating laser beams. In Figure 1, the product of the fraction of molecules ionized ($N_{ion}^+/N_{g,0}$) and the size of the detection volume (cm^3) is calculated. The product of this number and the molecular number density (cm^{-3}) gives the number of ions formed per lasershot. It is observed that for spotsizes below 200 μm , the two-photon transition is readily saturated at both laser powers, and the signal shows a quadratic dependence on the diameter of the detection volume. For a laser power of 0.5 mJ/pulse, the optimum efficiency is achieved for a waist of about 250 μm , whereas for a laser power of 1.0 mJ/pulse the optimum efficiency occurs around a waist of 380 μm . The theoretical detection efficiencies at these waists are $1.1 \cdot 10^3$ molecules/ cm^3 and $5.7 \cdot 10^2$ molecules/ cm^3 , respectively. As the waist is increased further, a situation is reached where the detection efficiency falls off quadratically with the diameter of the detection volume.

It should be stressed that the calculations given above assume that experimentally there are no mechanisms which broaden the bandwidth of the two-photon transition beyond the

bandwidth of the laser. As our experimental results will show, the (2+1) REMPI detection efficiency is in fact reduced by the occurrence of a dynamic Stark effect.

III. Experimental

The experimental set-up used in these measurements consists of a vacuum chamber in which two counterpropagating tunable ultra-violet laser beams are overlapped and focussed to a waist of several hundred μm . Ions produced by the lasers are accelerated and mass-selected by time-of-flight prior to detection using a position-sensitive ion detector. A detailed description will now be given of the laser system used and various elements in the experimental arrangement which are necessary to obtain the high sensitivity for the detection of hydrogen molecules.

The near transform-limited tunable laser system used in this experiment is based on pulse-amplification of the continuous output of a Coherent 699-29 Autoscan ringlaser in four stages using three prism dye amplifiers. In this amplifier chain, which is pumped by a 10 Hz Quatel Model YG-592 Nd:YAG laser, the second dye cell is double-passed. This laser is capable of delivering approximately 100 mJ of visible laser light in a 12 nsec pulse, with a near transform-limited bandwidth which was recently re-measured to be approximately 52 MHz. The detailed design of this laser system was published previously¹⁷.

In order to improve the spatial mode quality of the laser, the expanding telescope between the first (1 mm) and second (3 mm) dye amplifier was set up in such a way that the laser converged to a 2 mm spot at the entrance to the beam-expanding telescope between the second and third (6 mm) amplifier, where the beam size was increased by a factor three, rather than by a factor two, as in the design of Cromwell et.al. The use of a converging laser beam through the second dye amplifier reduces the appearance of diffraction rings, in particular on the second pass through this cell, giving a beam which can be amplified more homogeneously in the final amplifier, without any loss of power.

The visible output was doubled in KDP using an Inrad Autotracker II and separated from the resulting ultraviolet by using a dielectric mirror coated for 300 nm. The polarization of the residual visible light was rotated through 90° by using a double Fresnel rhomb and the visible and ultraviolet beams were recombined using another dielectric mirror coated for 300 nm. An $8 \times 8 \times 8 \text{ mm}^3$ BBO crystal cut at 74° was used to generate the tunable light around 201 nm, where laser powers up to 4.5 mJ/pulse were observed.

In order to focus the laser beam down to a waist of several hundred μm , a telescope was

used consisting of two 300 mm lenses which were set up to give a focus approximately 5 m downstream. For an ideal 6 mm Gaussian beam the size of the waist would be 60 μm . It was not expected that our laser would approach this value, and by applying a knife edge technique¹⁸⁾, the spotsize inside the vacuum chamber was in fact experimentally determined to be about 500 μm . At some wavelengths, for example near the $a^1\Sigma_g^+ \leftarrow X^1\Sigma_g^+$ two photon transition in the N_2 molecule¹⁹⁾, a spark was observed at the focus between the two 300 mm lenses. To alleviate this problem the first 300 mm lens will soon be replaced by a 200 mm negative focal length lens. At the same time this change is expected to reduce the focal spotsize by about 30 %, which might improve the detection efficiency, as can be seen from Figure 1.

After the telescope the 200 nm light was split into two beams of approximately equal power by using a 50/50 beamsplitter. The two laser beams were directed to the vacuum chamber using dielectric mirrors coated for 207 nm and 193 nm. The 207 nm mirrors were found to be preferable at angles of incidence of 45° and larger, whereas the 193 nm mirrors provided better reflectivity at points along the beamline where slightly smaller angles of incidence were required. Care was taken to avoid excessive transmission losses at any of the turning mirrors. Available 1 cm quartz prisms proved to give significant absorption and reflection losses.

The two vertically polarized counterpropagating lasers entered and exited the vacuum chamber through 5 mm thick Heraeus Amersil Suprasil CFQ Standard SVIA windows placed at Brewster's angle. In view of the high power density of the 201 nm beams, the windows were placed 1 m from the focus inside the vacuum chamber. In this configuration, the lasers could be operated for extended periods of time (approximately 100 hours) before any significant damage occurred. The windows could be rotated while the machine remained under vacuum.

The counterpropagating laser beams entered the central portion of the chamber after passing through a lightbaffle consisting of three skimmers made of anodized aluminum. While the first two skimmers had a 2 mm aperture, it was found that the aperture of the third skimmer needed to be increased to about 4 mm to avoid producing scattered light from the beam exiting the chamber on that particular side. Electrodes were placed behind the third skimmer in order to inhibit the acceleration of spurious photoelectrons towards the ion extraction region, but operation of the electrodes was not found to be necessary.

At the detector, the power density of the counterpropagating beams is approximately 10^8

W/cm², which is sufficient to non-resonantly dissociate and/or ionize a large number of background molecules within the duration of the laser pulse. Therefore it is crucial to apply mass selection to the ionized products. The ions were accelerated to a kinetic energy of approximately 1.5 kV over a 1 cm acceleration length. After entering a drifttube through a 90 % transmitting stainless steel mesh, they reached the detector following a 13.5 cm long drift length. The detector used in these experiments was a position-sensitive ion detector consisting of a 28 mm diameter dual microchannel plate amplifier (Hamamatsu F2224-21PFFX) followed by a P-20 phosphor screen held at +3 kV, and a fiberoptic coupler. The microchannel plates, which have a quantum efficiency of approximately 60 %, were operated by applying a 50 nsec long pulse of up to 1.8 kV to the anode surface, with the cathode surface being held at ground throughout. Thus the microchannel plate gain was only present during the arrival of the ion mass selected by the choice of the delaytime between the high voltage pulse for the microchannel plate and the Nd:YAG Q-switch pulse.

At the initial stage of these experiments, it was found that a substantial spurious signal arose from the formation of photoelectrons inside the field-free drifttube. These photoelectrons were formed by the laser and remained detectable with a 1/e decaytime of approximately 500 nsec. In order to eliminate this signal, the aforementioned light baffles were introduced, and, more importantly, the drifttube was held at a positive bias with respect to the microchannel plate cathode, thereby completely eliminating this problem. Somewhat surprisingly, it was found that a bias of as much as +60 V was required to inhibit the detection of these photoelectrons. This would seem to indicate that the cathode acquires a slightly positive voltage during the pulsing of the microchannel plates. After prolonged, successful operation of the microchannel plates some arcing problems were encountered between the microchannel plate anode and the phosphor screen. It is believed that this may be a side-effect of the pulsed operation of the microchannel plates.

The photon signal at the phosphor screen was imaged onto a Hamamatsu C3077 video camera by using a 4.3 : 1 demagnifying telescope. The video camera was interfaced to a Hamamatsu DVS 3000 image processor. At a clockrate of approximately 30 Hz video images are transferred and digitized. A discriminator level serves to filter out the thermal and/or readout noise associated with the operation of the camera. This ensures that there is no instrument-related

lower limit on the number of ions that is required for a detectable signal²⁰). In the experiments reported in this paper, spectra were recorded where by transferring video images accumulated on the image processor to an IBM PC, where the total signal intensity was calculated and stored.

In order to measure the detection efficiency of the (2+1) REMPI scheme, H₂ gas was admitted to the vacuum chamber until a change of $5 \cdot 10^{-7}$ Torr was observed on the Granville Phillips Bayard-Alpert ionization gauge. Under these conditions it was observed that with the detection laser 30 cm^{-1} detuned from the DH E,F($v=0, J=0$) \leftarrow X($v=0, J=0$) resonance, the background at the DH⁺ arrival time was less than one count per hundred lasershots. Consequently the *single shot* detection efficiency corresponds to the DH density where on average one DH⁺ ion is formed per lasershot.

The power dependence of the (2+1) REMPI process was determined by recording the (2+1) REMPI spectrum of H₂($J=1$) at a number of laser powers. The power of the 201 nm light was attenuated by turning down the voltage of the flashlamps in the Quantel YG 592 Nd:YAG laser which pumps the amplifier chain. This method of attenuation was chosen in order to preserve the mode and the alignment of the 201 nm beam as much as possible. Since the saturation of the dye amplifiers depends on the power of the Nd:YAG laser, some change in the mode of the 201 nm light is anticipated, however.

IV. Results

a) The power dependence of (2+1) REMPI of H₂(J=1)

In Figure 2 the (2+1) REMPI spectrum of H₂(v=0,J=1) is shown for three different laser powers. The laser power indicated in Figure 2 was measured between the first and the second 300 mm lens of the telescope which sets up the focussing of the counterpropagating beams. Consequently, this number is to be interpreted as a *relative* measure of the power density inside the vacuum chamber.

The power dependence of the (2+1) REMPI detection of H₂(v=0,J=1) is shown in Figure 3, where the signal intensity measured at the peak of the frequency spectrum is plotted versus the laser power. The power dependence follows a near-quadratic behaviour in the energy range from 1.5 to 3.2 mJ/pulse, whereas for energies below 1.5 mJ/pulse the signal drops off more rapidly. This is due to the fact that at lower energies the ionization step is not yet saturated. Figure 3 does not show any pronounced leveling-off of the power dependence towards higher pulse energies. We have on occasion seen preliminary evidence of this kind of behaviour, which would be indicative of the onset of saturation of the two-photon excitation step. In Figure 3 we have chosen to display a power dependence measurement which was carried out under the same conditions as existed during our calibration of the DH(v=0,J=0) detection efficiency, to be discussed below.

The spectra in Figure 2 show evidence of an AC Stark effect. As the laser power is increased both a shift and a broadening of the line profile is observed. The occurrence of an AC Stark effect is inherent in the use of a two-photon technique, since the same matrix elements which couple the ground and two-photon excited state to the virtual intermediate state, shift these states with respect to the intermediate state^{5,21}. Assuming a homogeneous laser spatial profile, one can calculate that with a total power of 1.2 mJ focussed to a 500 μm spotsize, the observed shifts of the two-photon transitions in Figure 2 are about 15 MHz per MW/cm². This value agrees reasonably well with a value of 3-6 MHz per MW/cm² estimated by Hessler²². Rhodes et.al.²³ have reported a shift of 45 cm⁻¹ in the E,F ¹Σ_g⁺ (v=2) <--- X¹Σ_g⁺ (v=0) transition frequencies using ArF excimer laser powers of 6 10¹¹ W/cm².

It is observed in Figure 2 that the AC Stark effect leads to a broadening of the linewidth beyond the laser linewidth, as well as an asymmetry of the lineshape. While the FWHM in the spectra recorded at 1.0 mJ/pulse and 1.5 mJ/pulse corresponds to the 150 MHz two-photon laser bandwidth, the FWHM of the main peak in the spectrum recorded at a laser power of 3.2 mJ/pulse is equal to about 550 MHz. As a result of this broadening of the molecular linewidth, the effective line shape function $g_{\text{effective}}(\omega)$ in Equations (5) and (6) approaches $g_M(\omega)$, and the numerical pre-factor in Equation (9), which was calculated using a 150 MHz two-photon bandwidth, will be reduced.

b) The ionization efficiency of DH(J=0) by (2+1) REMPI

A wavelength scan around the two-photon transition frequency for $\text{DH } E^1\Sigma_g^+(v=0, J=0) \leftarrow X^1\Sigma_g^+(v=0, J=0)$ is shown in Figure 4. This spectrum was recorded by admitting H_2 gas into the vacuum chamber until the ionization gauge recorded a pressure increase of $5 \cdot 10^{-7}$ Torr. Using the H_2 molecule sensitivity factor of 2.4 recommended by Summers²⁴⁾, the H_2 pressure in the vacuum chamber was therefore equal to $1.2 \cdot 10^{-6}$ Torr. The natural abundance of D isotopes is $1.5 \cdot 10^{-4}$ ²⁵⁾. Consequently, under these experimental conditions the pressure of DH in the vacuum chamber was equal to $3.6 \cdot 10^{-10}$ Torr. At room temperature about 20 % of the DH molecules are in the ground rotational state. Therefore the pressure of $\text{DH}(v=0, J=0)$ being probed was $7.2 \cdot 10^{-11}$ Torr. The laser power inside the vacuum chamber in both counterpropagating laser beams was about 0.6 mJ/pulse.

The spectrum shown in Figure 4 was recorded by accumulating video images for about 20 lasershots per point while scanning the two-photon frequency at a rate of 30 MHz/sec. At the maximum in Figure 1, the average number of DH^+ ions recorded per lasershot was equal to 190. As discussed in the experimental section, away from the two-photon resonance, the signal drops to less than one count per hundred lasershots. Therefore, a *single shot* signal-to-noise ratio of one would be obtained in a situation where on average one DH^+ molecule is detected per lasershot. This would be the case for a $\text{DH}(v=0, J=0)$ pressure of $3.8 \cdot 10^{-13}$ Torr, or a density of $1.2 \cdot 10^4$ $\text{DH}(v=0, J=0)/\text{cm}^3$.

In the present experiment, the signal is limited by the quantum efficiency of the position-

sensitive ion detector, which is about 60 % for the microchannel plates used. If this detector were to be replaced by a more efficient detector such as a scintillation detector²⁶, the quantum efficiency could be improved to almost 100 %. In addition, if it is taken into account that the mesh which separates the acceleration region from the drifttube has a 90 % transmission, the *single shot* detection limit for DH($v=0, J=0$) would be at a density of $6.8 \cdot 10^3$ molecules/cm³.

As discussed in the experimental section, the spotsize inside the vacuum chamber was determined to be approximately 500 μm . Using Equation (9) the theoretical detection sensitivity for DH($v=0, J=0$) under the conditions described above was calculated to be approximately $2.0 \cdot 10^3$ molecules/cm³. There are two reasons why our experimental detection efficiency is smaller than this value. First, the spatial mode of the 201 nm light is not very homogeneous, and this may lead to an imperfect overlap of the counterpropagating beams throughout the detection volume. More important however, as discussed above, the two-photon transitions are subject to a dynamic Stark effect which effectively broadens the molecular linewidth. Based on the observed FWHM of 550 MHz in Figure 2, it is expected that the upumping rate calculated using Equation (9) is too high by no less than a factor of four, and this readily accounts for the difference between the observed and the calculated detection efficiency.

V. Discussion

In this paper improved efficiencies have been reported for the detection of molecular hydrogen by the application of a (2+1) REMPI scheme through the E,F $^1\Sigma_g^+$ state, using two counterpropagating near transform-limited laser beams. With readily available laser powers, a *single shot* DH($v=0, J=0$) detection efficiency of $6.8 \cdot 10^3$ molecules/cm³ has been demonstrated. Not only is this comparable or better than the best detection efficiency which has been obtained using (1+1) xuv+uv REMPI, but due to the Doppler-free nature of the technique, this detection efficiency is independent of the velocity and angular distribution of the sample which is being probed.

In experiments involving state-specific spectroscopic product detection, a frequent problem is the fact that for many atoms and simple molecules the lowest optically accessible excited states are in the vacuum or extreme ultra-violet energy range. A choice has to be made between a multi-photon resonant excitation technique using ultraviolet lasers or a single-photon resonant excitation technique involving the use of coherent vacuum- or extreme ultraviolet laser light. While it is generally recognized that the generation of the light required in the multi-photon schemes is significantly easier, there is a consensus that the single-photon excitation schemes are more sensitive and that the resulting spectra are easier to analyze^{27,28}). We would like to present the argument that while single-photon excitation schemes are preferable in many applications, the individual details of an experiment determine which technique should be chosen.

The choice between a single- and a multi-photon excitation technique should be based on three criteria, namely, the sensitivity of the technique, the reliability of the obtainable experimental results, and the technical difficulty of the method. These criteria will now be discussed in turn.

In discussing the sensitivity of the single- and multi-photon excitation techniques, one of the most important factors is to consider the molecular and laser bandwidths involved in the experiment. The question that needs to be answered is to what extent the effective Dopplerwidth of the products to be detected limits the fraction of the products that can absorb within the bandwidth of the available laser system. If this fraction is significantly less than unity, the application of Doppler-free two-photon excitation may be appropriate.

For example, as demonstrated in this paper, with a near-transform limited laser, single- and two-photon excitation of hydrogen molecules are competitive as long as the Doppler width is smaller than the laser bandwidth or other contributions to the molecular bandwidth. If the Doppler width becomes larger, as is frequently the case in dissociation processes or reactions involving hydrogen molecules, the sensitivity of the single-photon xuv excitation drops dramatically, while the sensitivity of the (2+1) REMPI with counterpropagating beams is unaffected. Of course the sharp contrast that we observe under our experimental conditions between the detection efficiencies via (1+1) REMPI and (2+1) REMPI is a direct consequence of the use of a near transform-limited laser. In most laboratories, the bandwidth of the lasers used is significantly beyond the Fourier transform-limit, and the Doppler-free advantage may be lost. Also, since the mass of the hydrogen molecule is very light, the Doppler widths and the possible Doppler-free enhancements tend to be particularly large for hydrogen.

A second point which needs to be addressed is the reliability of the experimental results which can be obtained using single-photon and multi-photon resonant excitation schemes. A major advantage of the single-photon resonant techniques is the fact that extraction of the ro-vibrational population distributions is much easier using this method. Calculations of multi-photon transition moments are significantly more complicated than the evaluation of the Franck-Condon factors required when a single-photon resonant technique is used. For the case of the hydrogen molecule the situation is very fortuitous in that both for the one-photon excitation scheme²⁹⁾ and for the two-photon excitation scheme^{4,11)} extensive information on the line strengths is available.

It should be noted that in some experiments, a determination of the Doppler profile is one of the explicit goals. In experiments of this kind, a single-photon resonant or a single-beam multi-photon resonant technique will be preferable depending on whether the shot-to-shot fluctuations in the laser power are more pronounced in the vacuum ultraviolet generation or in the multi-photon excitation. In addition, in some experiments Doppler shifts can cause a non-uniform detection efficiency for different product angles and/or velocities. (2+1) REMPI with counterpropagating beams can be an appropriate way to circumvent these problems.

Technically, the single-photon and multi-photon resonant schemes both have advantages and disadvantages. While application of the multi-photon techniques is possible using conventional tunable laser systems, the single-photon excitation schemes require the sophistication

of the generation of coherent vacuum or extreme ultraviolet light. The price that one pays in the multi-photon excitation schemes is that these experiments tend to be more sensitive to background signals. In the case of the hydrogen molecule, the REMPI lasers need to be focussed down to $O(10^8 \text{ W/cm}^2)$. Not only does one need to worry about whether the REMPI laser will influence the molecular process under study, but at these high power densities, dissociation and/or ionization of background molecules can give additional signal. In our vacuum chamber, the background pressure is approximately 10^{-7} Torr, and without changing the apparatus, background-free detection would probably be limited to masses below $m=25$.

ACKNOWLEDGEMENTS

The authors wish to acknowledge Dr. K. Oba and M. Suyama of Hamamatsu Photonics, for the development of the position-sensitive ion detector.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

REFERENCES

- 1) For a review of these experiments see J.J. Valentini and D.L. Phillips, in "Advances in Gas-Phase Photochemistry and Kinetics - Bimolecular Collisions", edited by M.N.R. Ashfold and J.E. Baggott, (1989), p. 1-51.
- 2) M.J.J. Vrakking, A.S. Bracker and Y.T. Lee, Book of Abstracts, XIIIth International Symposium on Molecular Beams, El Escorial, Madrid, Spain, 2-7 June 1991.
- 3) A.H. Kung, T. Trickl, N.A. Gershenfeld and Y.T. Lee, Chem. Phys. Lett. 144, 427 (1988).
- 4) K.-D. Rinnen, D.A.V. Kliner, R.N. Zare and W.M. Huo, Isr. J. of Chemistry 29, 369 (1989).
- 5) N. Bloembergen and M.D. Levenson, in "High-Resolution Laser Spectroscopy", edited by K. Shimoda, Topics in Applied Physics Vol. 13, (Springer, 1976), p. 315-369.
- 6) See, for example
 - a) C. Zimmermann, R. Kallenbach and T.W. Hänsch, Phys. Rev. Lett. 65, 571 (1990).
 - b) L. Julien, F. Biraben, J.C. Garreau and M. Alleguini, Laser Spectroscopy IX, Proceedings of the Ninth International Conference on Laser Spectroscopy, Bretton Woods, New Hampshire, June 18-23 1991, p. 341.
 - c) S.A. Lee, S.J. Sternberg and L.U.A. Anderson, *ibid*; p. 382.
- 7)
 - a) S. Chu, A.P. Mills, Jr. and J.L. Hall, Phys. Rev. Lett. 52, 1689 (1984).
 - b) M.S. Fee, A.P. Mills Jr., E.D. Shaw, R.J. Chichester, D.M. Zuckerman, S. Chu and K. Danzmann, Phys. Rev. A 44, R5 (1991).
- 8) D.J. Kligler and C.K. Rhodes, Phys. Rev. Lett. 40, 309 (1978).
- 9) E.E. Marinero, R. Vasudev and R.N. Zare, J. Chem. Phys. 78, 692 (1983).
- 10) E.E. Eyler, J. Gilligan, E. McCormack, A. Nussenzweig and E. Pollack, Phys. Rev. A 36, 3486 (1987).
- 11)
 - a) W.M. Huo, K.-D. Rinnen and R.N. Zare, J. Chem. Phys. 95, 205 (1991).
 - b) K.-D. Rinnen, M.A. Buntine, D.A.V. Kliner, R.N. Zare and W.M. Huo, J.

- Chem. Phys. 95, 214 (1991).
- 12) a) N. Bjerre, R. Kachru and H. Helm, Phys. Rev. A 31, 1206 (1985)
 - b) E.Y. Xu, H. Helm and R. Kachru, Phys. Rev. A 39, 3979 (1989).
 - 13) a) W.L. Glab and J.P. Hessler, Phys. Rev. A. 35, 2102 (1987); *ibid* 42, 5486 (1990).
 - b) W.L. Glab and J.P. Hessler, Phys. Rev. Lett. 62, 1472 (1989).
 - 14) For a review of the perturbation theory for one- and two-photon transitions see W.M. McClain and R.A. Harris in "Excited States", Vol. 3, edited by E.C. Lim, (Academic, 1977), p. 1-56.
 - 15) D. Kligler, J. Bokor and C.K. Rhodes, Phys. Rev. A 21, 607 (1980).
 - 16) a) E.F. Cromwell, PhD thesis, University of California at Berkeley (1991).
 - b) E.F. Cromwell, private communication.
 - 17) E. Cromwell, T. Trickl, Y.T. Lee and A.H. Kung, Rev. Sci. Instrum. 60, 2888 (1989).
 - 18) J.M. Khosrofian and B.A. Garetz, Appl. Opt. 22, 3406 (1983).
 - 19) a) K.R. Lykke and B.D. Kay, J. Chem. Phys. 95, 2252 (1991).
 - b) M.J.J. Vrakking, A.S. Bracker and Y.T. Lee, J. Chem. Phys. 96, 7195 (1992).
 - 20) R.A. Wick, BioTechniques 7, 262 (1989).
 - 21) P.F. Liao and J.E. Bjorkholm, Phys. Rev. Lett. 34, 1 (1975).
 - 22) J.P. Hessler, private communication.
 - 23) a) T. Srinivasan, H. Egger, H. Pummer and C.K. Rhodes, I.E.E.E. Journal of Quantum Electronics, QE-19, 1270 (1983).
 - b) H. Pummer, H. Egger, T.S. Luk, T. Srinivasan and C.K. Rhodes, Phys. Rev. A 28, 795 (1983).
 - 24) R.L. Summers, NASA Technical Note TN D-5285.
 - 25) CRC Handbook of Chemistry and Physics.
 - 26) N.R. Daly, Rev. Sci. Instrum. 31, 264 (1960).
 - 27) J.W. Hepburn, in "Vacuum Ultraviolet Photoionization and Photodissociation of Molecules and Clusters", edited by C.Y. Ng (World Scientific, 1991); p: 435-485.
 - 28) A.H. Kung and Y.T. Lee, *ibid.*, p. 487-502.
 - 29) H. Abgrall, F. Launay, E. Roueff and J.-Y. Roncin, J. Chem. Phys. 87, 2036 (1987).

FIGURE CAPTIONS

- Figure 1 The dependence of the detection sensitivity on the size of the laser focus. The number plotted on the left is the product of two-photon transition probability and the size of the detection volume (cm^3). See text for details.
- Figure 2 Frequency spectrum of (2+1) REMPI of $\text{H}_2(\nu=0, J=1)$ at laser powers of 1.0 mJ/pulse, 1.5 mJ/pulse and 3.2 mJ/pulse. These laser powers were measured between the two 300 mm lenses of the telescope for the 201 nm light. The two-photon transition frequencies are obtained by adding 99100 cm^{-1} to the relative transition frequencies shown.
- Figure 3 Double-log plot of the power dependence of (2+1) REMPI of $\text{H}_2(\nu=0, J=1)$. The laser powers were measured between the two 300 mm lenses of the telescope for the 201 nm light.
- Figure 4 Frequency spectrum of (2+1) REMPI of $\text{DH}(\nu=0, J=0)$. The transition frequency is obtained by adding 99300 cm^{-1} to the relative transition frequency shown.

Dependence of detection sensitivity on laser focus

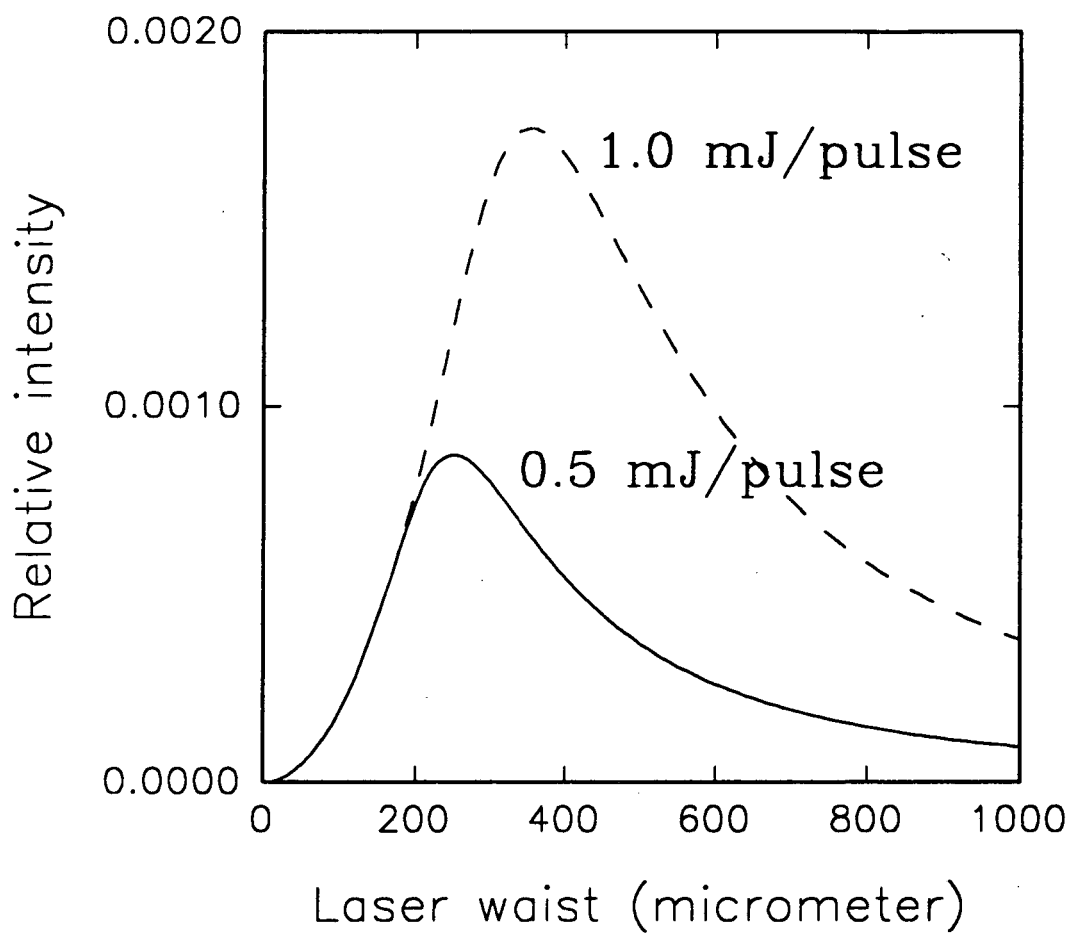


Figure 1

Power dependence for (2+1) REMPI
of $H_2(v=0, J=1)$

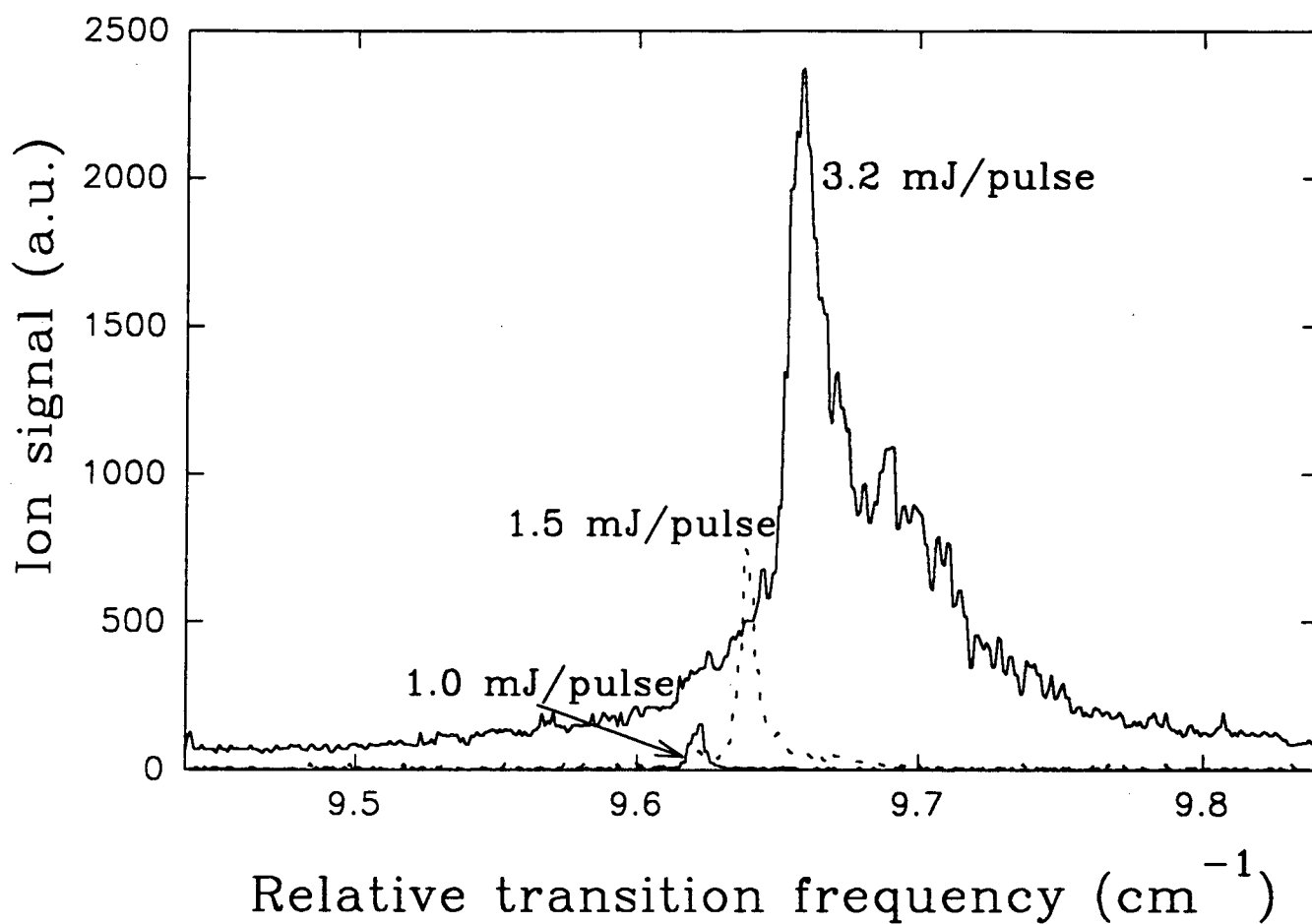


Figure 2

Power dependence of (2+1) REMPI

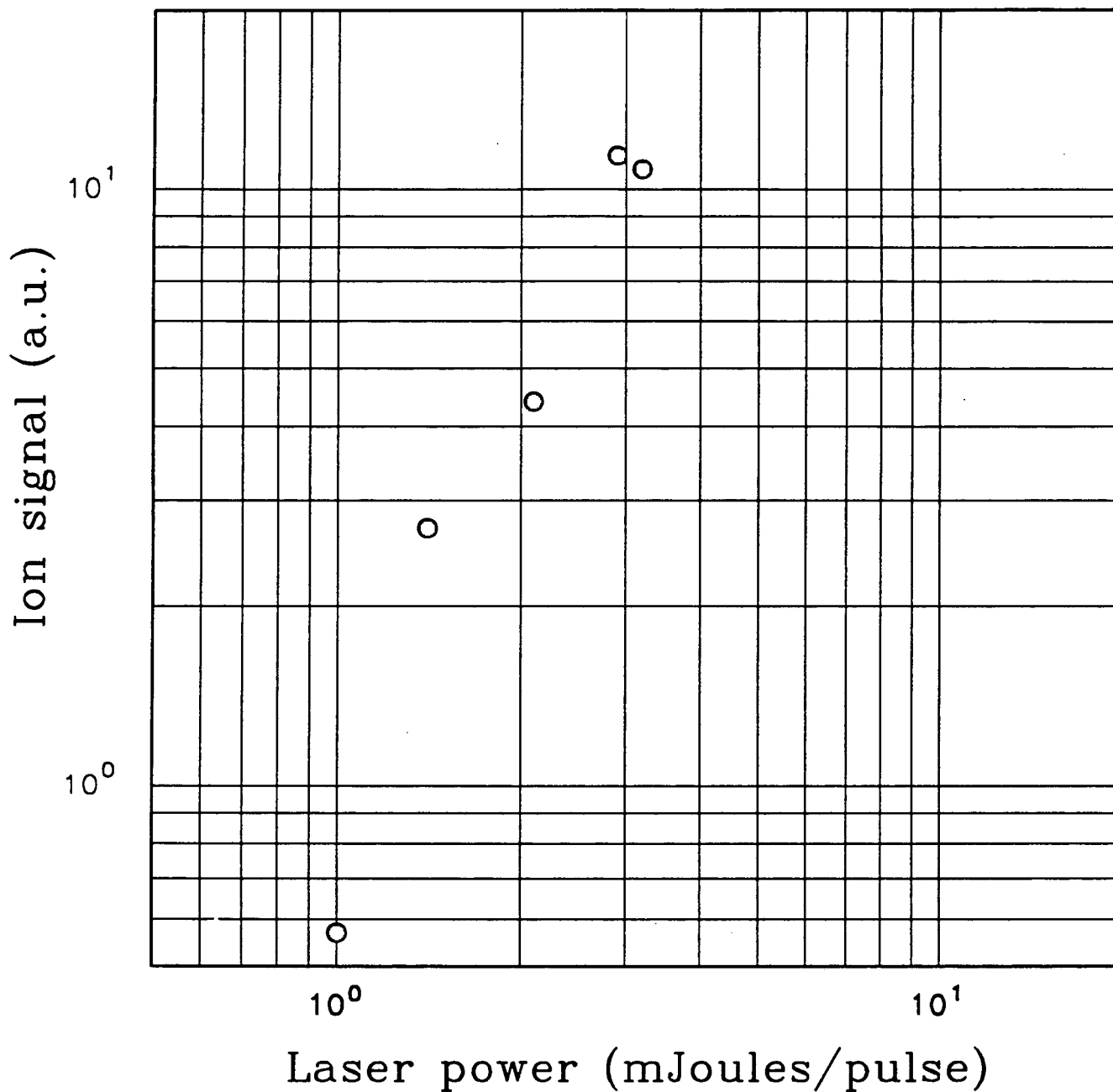


Figure 3

Detection of $\text{DH}(\nu=0, J=0)$ by (2+1) REMPI

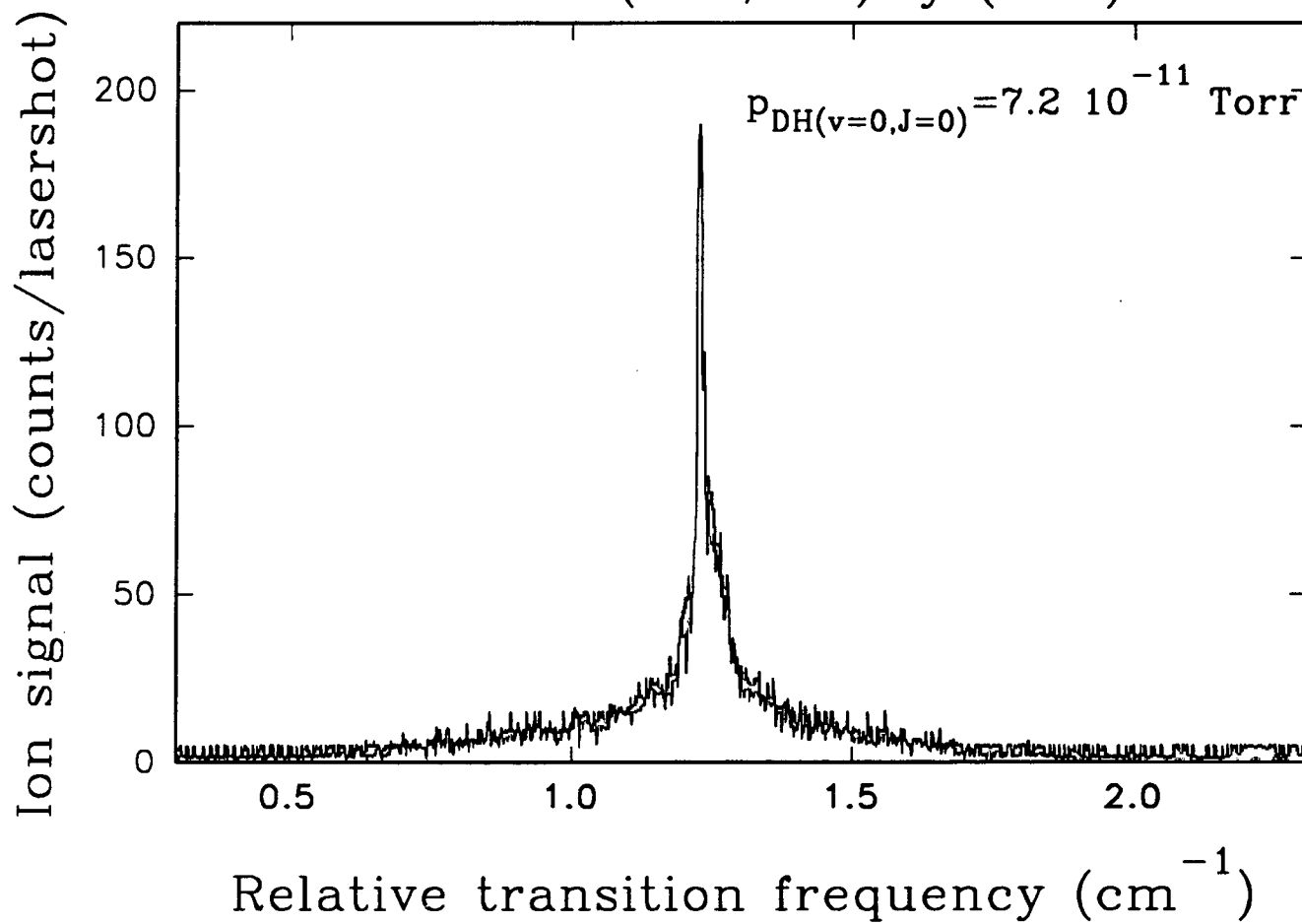


Figure 4

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720