J. Phys. Chem. A **1998,** *102,* 6063−6067

One-Color Molecular Photodissociation and Detection of Hydrogen Atoms

Robert Quandt, Xuebin Wang, Zhiyuan Min, Hong Lae Kim,[†] and Richard Bersohn*

Department of Chemistry, Columbia University, New York, New York 10027

Received: January 23, 1998; In Final Form: April 14, 1998

The wavelength 205.14 nm is absorbed by many hydrogen-containing molecules, which then dissociate to form hydrogen atoms. These in turn can absorb two more 205.14 nm photons and reach the 3s or the 3d state. They can absorb a third photon and form hydrogen ions or decay to the ground state by stepwise fluorescence, first emitting the Balmer α line at 656.2 nm (3s or 3d→2p)and then the Lyman α line (2p→1s)at 121.6 nm. Thus the hydrogen atom kinetic energy can be probed in three different ways. This method broadens greatly the possibilities of investigating photodissociations leading to hydrogen atom products. It has the advantage of simplicity and the disadvantages of a single-color experiment. The method is tested with a molecule that has been extensively investigated, H_2S, and then applied to three other molecules, formic acid (HCO_2H), vinyl radical (C_2H_3), and allyl radical (C_3H_5). H_2S has a perpendicular transition with a large release of kinetic energy. Studies of the latter molecules lead to the conclusion that formyl, carboxyl, vinyl, and allyl radicals absorb 205.1 nm light and release hydrogen atoms with a large fraction of the available energy. The dissociation pathways of formic acid are clarified.

Hydrogen atoms can be detected by electron spin resonance or by the consequences of electronic absorption. The most commonly used transition is from the 1s to the 2p state at 121.6 nm.[1−3] The absorption can be measured by detecting the VUV fluorescence back to the ground state or by detecting hydrogen ions formed by absorption of an additional UV photon. A variation of the latter method due to Welge and Ashfold uses excitation to the 2p state followed by further excitation to a high Rydberg state just below the ionization energy. The hydrogen atom in this state is ionized by an electric field at the end of a drift tube.[4]

An alternative method is based on simultaneous rather than consecutive two-photon absorption. Focused 243.2 nm light can excite a 1s to 2s transition. This paper describes one more variation used by Goldsmith in connection with flame diagnostics, namely, the two-photon absorption of 205.14 nm light.[5,6] This method has also been used by Meier et al.[7] as a diagnostic tool for H atoms in diamond synthesis. In this method hydrogen atoms are excited partly to the 3s but mainly to the 3d state.[8] There are several advantages. Many molecules that are transparent or only weakly absorbing at 243.2 nm absorb well at 205.14 nm, greatly expanding the possibilities of studying their photochemistry. Also three techniques exist for detection: (a) ionization by absorption of an additional photon, (b) Balmer α fluorescence (3d or 3s→2p) at 656.6 nm, and (c) Lyman α fluorescence (2p→1s) at 121.6 nm. The relevant transitions are shown in the energy level diagram of Figure 1. Finally, the high frequency of the transition, 97 466 cm^{-1}, increases the Doppler width and hence the accuracy of line shape determination.

This paper presents several examples of simple one-color experiments in which a 205.14 nm photon is used to dissociate a molecule and two additional photons are absorbed to probe the resulting hydrogen atom. To test the method, the first study was on a molecule, H_2S, whose photodissociation has been extensively investigated. Then, three much less studied systems, formic acid, vinyl radical, and allyl radical, were studied. The great advantages of a one-color experiment in which the pump and probe are identical and some of its limitations are discussed.

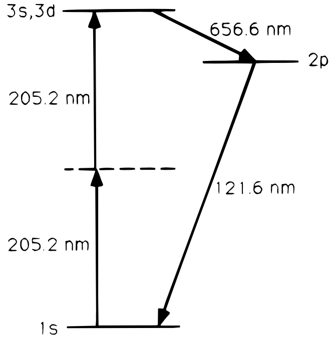

Figure 1. Energy levels of the hydrogen atom showing the two-photon transition and the Lyman α and the Balmer α transitions.

Experimental Section

Light of 615.42 nm was generated by a Continuum ND-60 YAG pumped dye laser using Rhodamine 640 and a small amount of DCM dye. The red light was frequency doubled in a KDP crystal, and the resulting doubled frequency light was mixed with the fundamental in a BBO crystal (type I cut at 73°) to produce 1.2 mJ/pulse at 205.14 nm. A Pellin-Broca system of four prisms separated the third harmonic from the fundamental and second-harmonic radiation. This light was focused with an 8 cm focal length quartz lens through the quartz window of a cell containing a gas flowing at a pressure of about 100 mTorr. An INRAD Autotracker was used to maximize mixing in the BBO crystal. The efficiency of frequency tripling was a sharp function of the crystal angles. Optimization with the Autotracker was therefore a necessity, but the intensity did oscillate somewhat during the scan across the absorption. VUV fluorescence was detected by a solar blind EMR 542G-08-17

[†] Permanent address: Department of Chemistry, Kangweon University, Chuncheon 200-701, Korea.

S1089-5647(98)00877-3 CCC: $15.00

TABLE 1: Translational Energy Release on Photodissociation

molecule	H−SH	C_2H_2−H	D-CO−OH	D-CO_2−H	CH_2CHCH_2
D_0 (kJ/mol)	376.4[a]	144[b]	527[c]	425[c]	243[d]
$E_{AVL} = h\nu - D_0$	206.9	439	639*	741*	340
$\langle E_T\rangle$	196 ± 3	189 ± 27	302 ± 20(D)	218 ± 40(H)	139 ± 17
$f_T = \langle E_T\rangle/E_{AVL}$	0.95 ± 0.01	0.43 ± 0.06	0.47 ± 0.03	0.29 ± 0.05	0.41 ± 0.05

[a] Ref 4. [b] *CRC Handbook of Chemistry and Physics*; Lide, D. A. Ed.; CRC: Boca Raton, 1994. [c] *Photochemistry of Small Molecules*; Okabe, H. Wiley-Interscience: New York, 1978. [d] Ref 20. [e] At 205.14 nm, $h\nu$ is equivalent to 583.3 kJ/mol. *$E_{AVL} = 2h\nu - D_0$.

photomultiplier tube, and the red emission was detected with an RCA C31000M photomultiplier using an interference filter centered at 656 nm with a maximum transmission of 60% and a fwhm of 10 nm.

Results

Angular Distributions. If θ is the angle between the velocity vector of a photofragment and the electric vector, E, of the dissociating light, the angular distribution of fragments is given by the expression

$$f(\theta) = (1/4\pi)\{1 + \beta P_2(\cos\theta)\} \qquad (1)$$

where $\beta = +2$ for a parallel transition, 0 for an isotropic distribution, and -1 for a perpendicular transition. Suppose that the probe direction makes an angle $\theta_{P,E}$ with the E vector of the dissociating light. The angular distribution of the fragments with respect to the probe direction is now

$$f(\theta_{v,P}) = (1/4\pi)\{1 + \beta P_2(\cos\theta_{P,E})\, P_2(\cos\theta_{P,v})\} \qquad (2)$$

where $\theta_{P,v}$ is the angle between the direction of the probe and the velocity of the fragment. In the present case where the probe is always perpendicular to the E vector of the dissociating light because the pump and probe are identical, $P_2(\cos\theta_{P,E}) = -1/2$ and

$$f(\theta_{P,v}) = (1/4\pi)\{1 - (\beta/2)P_2(\cos\theta_{P,v}\}\} \qquad (3)$$

A Doppler-broadened spectrum extends symmetrically around the center frequency, ν_0 from $-v\nu_0$/c to $+v\nu_0$/c, where v is the magnitude of the velocity vector and c is the speed of light. In the present case ν_0 is 97 466 cm^{-1}. The Doppler spectrum extends from $\theta_{P,v} = 0$ to π. The average relative kinetic energy release of the two photofragments is obtained from the second moment of the excitation spectra using the formula

$$\langle E_T\rangle = (m_{RH}/m_R) < (\Delta v/v_0)^2 > 3mc^2/2 \qquad (4)$$

where m_H, m_{RH}, and m_R are the masses of the hydrogen atom, the molecule being photodissociated, and the partner fragment of the H atom, respectively. c is the velocity of light. In deriving eq 4 the fine structure splittings of the 3s and 3d states have been neglected. The 3^2S state lies 0.098 cm^{-1} below the $3^2D_{3/2}$ state, but under two-photon excitation it is only 12% occupied.[13] The $3^2D_{5/2}$ state is only 0.036 cm^{-1} above the $3^2D_{5/2}$ state. The experimental second moments are not accurate enough to justify the very small correction for the fine structure splitting. Results for the kinetic energy release are given in Table 1.

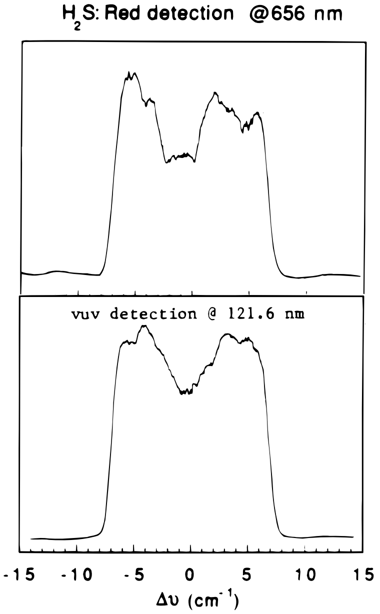

Figure 2. Doppler-broadened fluorescence excitation spectra of hydrogen atoms dissociated from H_2S at 205.14 nm. The balmer α and Lyman α excitation spectra are shown in the upper and lower panels, respectively.

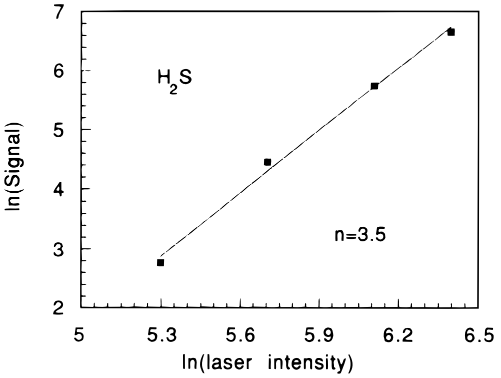

Figure 3. Plot of the ln of the red fluorescence signal intensity vs ln of the laser intensity. A minimum of three photons are required to excite the fluorescence, which is consistent with the slope of 3.5 ± 0.5.

Figure 2 shows the Doppler-broadened fluorescence excitation spectra for 121.6 nm emission and 656.6 nm emission of H atoms dissociated from H_2S. They are the same, reflecting the sequential nature of the 3s or 3d decay to the 2p state followed by the 2p to 1s decay. Figure 3 is a ln−ln plot of the fluorescence intensity versus the 205.14 nm intensity. The slope is 3.5 ± 0.5 with the uncertainty being a consequence of the fluctuations in laser intensity. The figure is consistent with a requirement of three 205 nm photons being required to produce the fluorescence. However, because of the steep dependence of the signal on laser intensity, it is not possible to vary the laser intensity over a wide range.

Figure 4 shows the VUV fluorescence excitation spectra of H_2S. The spectrum is broad and clearly entirely due to a transition in which the transition dipole is perpendicular to the hydrogen atom velocity direction. The fit with the theoretical spectrum is described below.

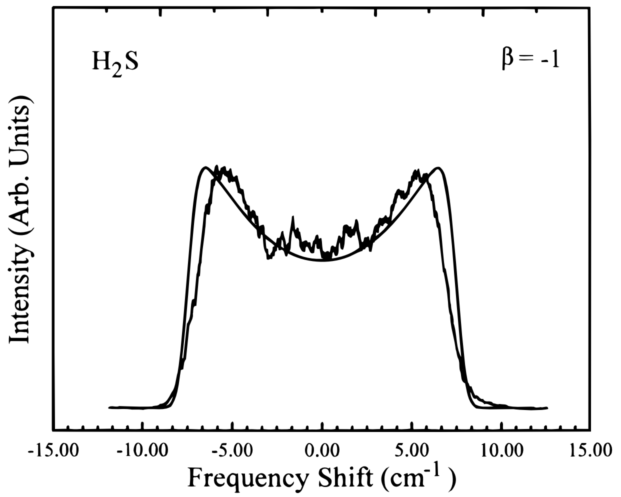

Figure 4. Balmer α excitation spectrum of H atoms photodissociated from H_2S at 205.14 nm. The solid line is a theoretical curve calculated for $\beta = -1$ and convoluted with a Gaussian laser function with fwhm of 1.0 cm^{-1}.

Discussion

H_2S Photodissociation. Hydrogen sulfide photodissociation in its first absorption band has been studied in a number of laboratories.[4,10,11] A 3pπ electron on the S atom is promoted to an antibonding σ state. A theoretical problem is that this state is of a_1 type, which should lead to symmetric excitation of both S−H bonds but not dissociation. Kulander has shown that strong coupling of the initially excited $^1B_1$ state with a neighboring dark $^1A_2$ state would result in excitation of the antisymmetric stretching mode and thence dissociation.[12] Xie et al. have shown that the SH fragment is indeed formed in vibrationally excited states but that the vibrational excitation decreases with decreasing available energy.[4] In particular at 205 nm they found the percentages of SH radicals in the $v = 0$, 1, 2, 3 states were 84.1, 8.8, 5.8, 1.3, respectively. The calculated spectrum shown in Figure 4 is a weighted superposition of four curves, each with $\beta = -1$ but with speeds calculated taking into account the vibrational state of the accompanying SH fragment.

Vinyl Bromide Photodissociation. The photodissociation of a molecular beam of vinyl bromide at 193.3 nm has been studied by Wodtke et al.[13] They found two channels:

$$C_2H_3Br + h\nu \rightarrow C_2H_3 + Br \qquad (5)$$

$$C_2H_3Br + h\nu \rightarrow C_2H_2 + HBr \qquad (6)$$

with a relative yield of 1.28 ± 0.05. They found no evidence of a third channel:

$$C_2H_3Br + h\nu \rightarrow C_2H_2Br + H \qquad (7)$$

If a 205 nm photon is used, the available energy in the process of eq 7 would be 121 kJ/mol. This would be an upper limit to the kinetic energy of the H atom. The average kinetic energy obtained with 205 nm photons was 182 ± 27 kJ/mol; thus, the one-step formation of H atoms is unimportant. The source of the H atoms is therefore a secondary photodissociation of the vinyl product of eq 5 or the HBr product of eq 6 or both. (Independent experiments with acetylene gave no H atom signal presumably because it has only a very weak absorption at 205 nm.) When cold HBr and C_2H_3 are photodissociated at 205.1 nm, the available energies are 221 and 444 kJ/mol, respectively.

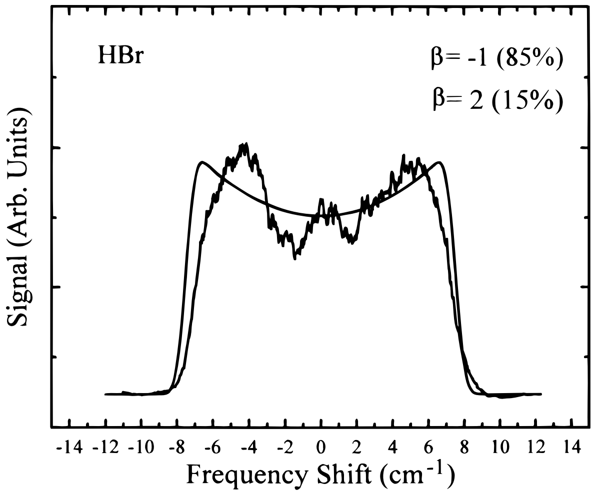

Figure 5. Same as Figure 4 except with HBr. The spectrum is mainly due to a perpendicular transition producing Br atoms in their lowest energy state.

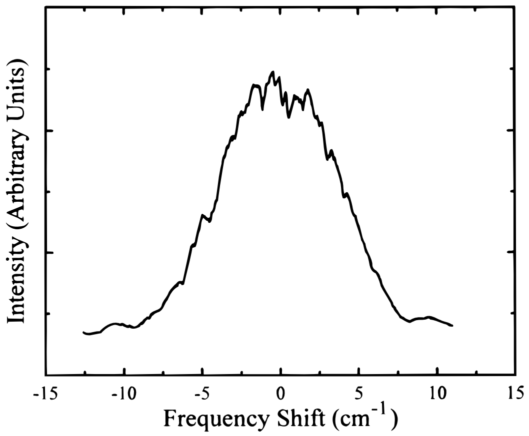

Figure 6. Balmer α excitation spectrum of the H atoms from vinyl bromide. The H atoms are derived from both HBr and C_2H_3. Note that it differs in shape from that of HBr as shown in Figure 5.

For HBr the assumption has been made that most of the Br atoms are formed in their lowest $4^2P_{3/2}$ state. Because HBr is a possible product of the first absorption, HBr was also used as a target molecule for the 205.1 nm light. The resulting Balmer α excitation spectrum is shown in Figure 5. The HBr spectrum is due to a mainly perpendicular transition producing ground-state Br atoms, consistent with what has been found in earlier experiments on HBr at 193 nm.[14,15] The shapes of the LIF excitation spectra shown in Figure 5 and that derived from vinyl bromide shown in Figure 6 are not the same, showing that if HBr is present, it must be mixed with vinyl radicals. If vinyl radical is a major product, as seems clear, most of the available energy in its dissociation energy must be released as internal vibrations. By a coincidence, two photoproducts, vinyl and HBr, release about the same amount of average translational energy when they are further dissociated at 205 nm. With this single-color method, we cannot, unfortunately, go further in analyzing this interesting process. A TOF experiment would accurately determine the relative importance of the two channels.

Formic Acid Photodissociation. When formic acid was dissociated at 205.1 nm, an LIF spectrum (Figure 7) was obtained with an odd shape resembling the superposition of two Doppler-broadened spectra, a strong central curve with considerable kinetic energy and a weaker curve with even more kinetic energy. To try to sort out what was happening, a sample of DCOOH was photodissociated at 205.14 and 205.09 nm. The

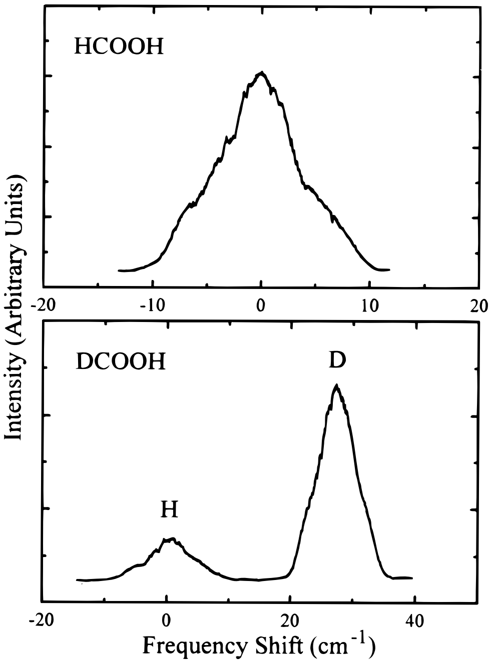

Figure 7. Balmer α excitation spectrum of hydrogen atoms from HCOOH (upper panel) and DCOOH (lower panel). Note that the spectrum of HCOOH appears to be the superposition of two spectra.

former wavelength dissociates the molecule and then excites H atoms; the latter dissociates and then excites D atoms. The average kinetic energies of the H and D atoms are 218 ± 40 and 289 ± 20 kJ/mol, respectively. The ratio of the areas under the D and H atom excitation curves is 4.11 ± 0.20.

The first absorption band of formic acid is a weak n→π^* transition peaking at 210 nm with an $\epsilon_{\max}$ of 37 M^{-1} cm^{-1}. Carbonyl compounds of the form RCOR′ (ketones and aldehydes) when electronically excited in the n→π^* region decompose either to R + R′CO or R′ + RCO. Either of the acyl compounds may have enough internal energy to dissociate so that the observed products may be R, R′, and CO. By analogy, in the case of formic acid we would expect that the following channels would be observed:

$$\mathrm{DCOOH} + h\nu \rightarrow \mathrm{DCO} + \mathrm{OH} \qquad E_{\mathrm{AVL}} = 121 \text{ kJ/mol} \tag{8}$$

$$\mathrm{DCOOH} + h\nu \rightarrow \mathrm{D} + \mathrm{HOCO} \qquad E_{\mathrm{AVL}} = 200 \text{ kJ/mol} \tag{9}$$

E_{AVL} is the photon energy $h\nu$ minus the amount of energy required for the dissociation into fragments with no translational or internal energy. Singleton et al. found that the quantum yield of process 8 for nondeuterated formic acid at 222 nm was 0.70 ± 0.05.[17] The nature of the other channel(s) remains obscure. The molecular elimination channels, CO + H_2O and CO_2 + H_2, are energetically allowed but are mechanistically implausible.

The major channel, reaction 8, does not produce D atoms in one step, but the formyl radical requires only 60 kJ/mol to dissociate into CO and D. However, its decomposition after the absorption of only one quantum cannot be the major source of H atoms. The available energy for the channel, DCO and OH, would be only 121 kJ/mol. Consistent with this small amount of energy is the finding in two separate studies, albeit at longer wavelengths, that the nascent OH is only in the $v = 0$ state and has only a little rotational energy. The average kinetic energy of the D atoms and its partner radical from DCOOH is 303 kJ/mol. Our conclusion is that the D atoms are mainly derived from the absorption of one more 205.1 nm photon by DCO. In other words the rate of uppumping is faster than the rate of dissociation. Tjossem et al. have measured a strong, structured 2+1 REMPI spectrum near 205 nm of jet-cooled DCO, but exactly at 48 474 cm^{-1} the absorption is weak.[16] The present case is somewhat different in that the DCO is likely to be hot and therefore more strongly absorbing. D atoms are also produced directly from reaction 9.

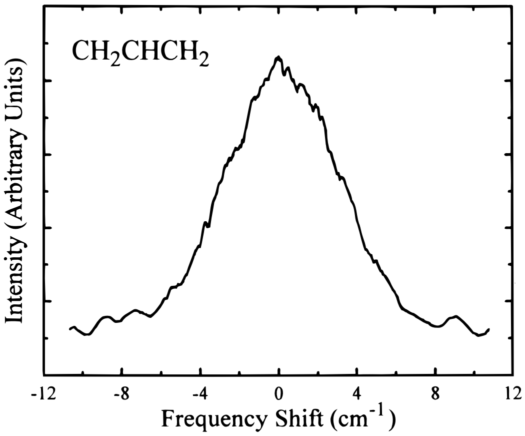

Figure 8. Balmer α excitation spectrum of H atoms from allyl bromide, CH_2CHCH_2Br. The source of the H atoms is the allyl product of the first absorption.

The source of the H atoms from the photodissociation of DCOOH must be the carboxyl radical, HOCO, from reaction 9. While it only requires 33 kJ/mol to dissociate HOCO into H + CO_2, the resulting H atoms would have less than the observed energy of 218 kJ/mol given that the D atom also has some energy. We come to the same conclusion as with DCO, that the HOCO molecule must absorb another 205.1 nm photon in order to produce the fast H atoms observed. The absorption spectrum of HOCO has not been measured in the vicinity of 205 nm, but it is plausible that it should absorb there and release hydrogen atoms. If we assume that reactions 8 and 9 are the only appreciable channels and that the branching ratio does not vary with isotope, then the D/H ratio of 4.11 ± 0.20 implies a quantum yield of 0.76 ± 0.01, in agreement with the value found by Singleton et al. at 222 nm.[17]

The principal findings on the photodissociation of formic acid are that the H + HOCO channel accounts for about 25% of the yield. However, both the HCO and HOCO products are cleaved by the same radiation that produces them from their precursor.

Allyl Radical Photodissociation. Allyl radical was generated by the irradiation of allyl bromide at 205.1 nm. The radical prepared in this way has an unknown but substantial amount of internal energy. However, both the rotational energy and the vibrational energy that is distributed over 18 vibrational modes are only weakly coupled to the dissociation coordinate. It is therefore likely that the H atoms generated from photodissociation of this hot radical will be only a little faster than those from a cold radical. The average translational energy release in this photodissociation calculated from the excitation spectrum of Figure 8 is 139 ± 17 kJ/mol. The process

$$\mathrm{CH_2{-}CH{=}CH_2} \rightarrow \mathrm{CH_2{=}C{=}CH_2} + \mathrm{H} \tag{10}$$

requires 243 kJ/mol, which means that the available energy at 205.1 nm is 340 kJ/mol. Therefore, the fraction of available energy released as translational energy is $f_{\mathrm{T}} = (139 \pm 17)/340 = 0.41 \pm 0.05$. In contrast, Deyerl et al. generated allyl radicals by pyrolysis and subsequent cooling by expansion. When photodissociating these cold radicals at 248 nm, they found an f_T value of 0.23.[20] The latter figure is consistent with dissociation from a hot ground state in which the available energy goes mostly to vibrations. Our fraction is much too high for a ground-state path. Instead it appears to be a result of a descent on a steeply repulsive surface from an initially excited Rydberg state. Support for this assumption comes from ab initio calculations that predict that in allyl transitions near 6.0 eV will be to Rydberg states.[21]

Summary

A two-photon absorption method for detecting hydrogen atoms previously used by Goldsmith and Meier for diagnostics has been applied to photodissociation processes. It produces strong fluorescence signals and obviates the need for generating VUV light. A birds-eye view of a photodissociation that releases hydrogen atoms is quickly obtained. When used in a one-color experiment, it has the disadvantage of inflexibility; the probe is always perpendicular to the polarization. While the focusing need not be extreme, the 205.1 nm excitation may dominate an excitation process caused by another wavelength. A well-studied molecule, H_2S, was used to test the method. Less familiar molecules, the radicals, vinyl, formyl, carboxyl, and allyl, all appear to absorb at 205 nm and to release fast hydrogen atoms.

Table 1 sumarizes the results obtained. Particularly revealing is the bottom row that lists the fractions of the available energy released as translation. The triatomic H_2S releases almost all the available energy as translation. The next highest value of f_T is for D from DCO_2H, which is mainly from the dissociation of the triatomic DCO. The other three dissociation processes in which vinyl is changed into acetylene, allyl into allene, and carboxyl into carbon dioxide all involve the breaking of a σ bond and the making of a π bond. These processes are *local* in that the atom making the new π bond is simultaneously breaking away from, i.e., repelling, the hydrogen atom.

Note Added in Proof: Langford, S. R.; Batten, A. D.; Kono, M.; Ashfold, M. N. R. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3757 report parallel but much more precise results on formic acid at somewhat longer wavelengths.

Acknowledgment. Thanks are due to the U.S. National Science Foundation (R.B.) and the Korea Research Foundation (H.L.K.) for financial support of this work.

References and Notes

(1) Wallenstein, R. *Opt. Commun.* **1980**, *33*, 119.

(2) Schmiedl, R.; Dugan, H.; Meier, W.; Welge, K. H. *Z. Phys. A* **1980**, *304*, 137.

(3) Johnston, G.; Park, J.; Satyapal, S.; Shafer, N.; Tsukiyama, K.; Bersohn, R.; Katz, B. *Acc. Chem. Res.* **1990**, *23*, 232.

(4) Xiu, X.; Schnieder, L.; Wallmeier, H.; Boettner, R.; Welge, K. H.; Ashfold, M. N. R. *J. Chem. Phys.* **1990**, *92*, 1608.

(5) Goldsmith, J. E. M. *Opt. Lett.* **1986**, *11*, 416.

(6) Goldsmith, J. E. M. *J. Opt. Soc. Am. B* **1989**, 1979.

(7) Meier, U.; Hohse-Honinghaus, A.; Schafer, L.; Klinges, C. P. *App. Optics* **1990**, *29*, 499.

(8) Goldsmith, J. E. M.; Rahn, L. E. *Opt. Lett.* **1990**, *15*, 814.

(9) Van Veen, G. N. A.; Mohammed, K. A.; Baller, T.; deVries, A. E. *Chem. Phys.* **1983**, *74*, 261.

(10) Johnston, G. W.; Katz, B.; Tsukiyama, K.; Bersohn, R. *J. Phys. Chem.* **1987**, *91*, 5445.

(11) Person, M. D.; Lao, K. Q.; Eckholm, B. J.; Butler, L. J. *J. Chem. Phys.* **1989**, *91*, 81.

(12) Kulander, K. C. *Chem. Phys. Lett.* **1984**, *103*, 373.

(13) Wodtke, A. M.; Hintsa, E. J.; Somorjai, J.; Lee, Y. T. *Isr. J. Chem.* **1989**, *29*, 383.

(14) Magnotta, F.; Nesbitt, S. R.; Leone, S. R. *Chem. Phys. Lett.* **1981**, *83*, 21.

(15) Xu, Z.; Koplitz, B.; Wittig, C. *J. Chem. Phys.* **1987**, *87*, 1062.

(16) Tjossem, P. J. H.; Cool, T. A.; Wells, D.; Grant, E. R. *J. Chem. Phys.* **1988**, *88*, 617.

(17) Singleton, D. L.; Parakevopoulos, G.; Irwin, R. S. *J. Photochem.* **1987**, *37*, 209; *J. Phys. Chem.* **1990**, *94*, 695.

(18) Ebata, T.; Fujii, A.; Amano, T.; Ito, M. *J. Phys. Chem.* **1987**, *91*, 6095.

(19) Brouard, M.; O'Mahony, J. *Chem. Phys. Lett.* **1988**, *149*, 45.

(20) Beyerl, H.-J.; Gilbert, T.; Fischer, I.; Chen, P. *J. Chem. Phys.* **1997**, *107*, 3329.

(21) Ha, T.-K.; Baumann, H.; Oth, J. F. M. *J. Chem. Phys.* **1986**, *85*, 1438.