A 1+1 Ionization Scheme for Sensitive Detection of the OH Radical†

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We introduce a new laser detection scheme for the OH radical that employs 1+1 $X^2\Pi \rightleftharpoons D^2\Sigma^-$ resonance enhanced excitation to a high-lying Rydberg state followed by field ionization. We place an upper limit of 8 ns on the lifetime of the $D^2\Sigma^-$ state. We also correct published values for T_0 for the $D^2\Sigma^-$ state, provide a new value for the energy of the $6s^1 11p^1\ ^3P_1^0$ state of Hg (81 807.6 cm^{-1}), and measure the rotational temperature of OH radicals produced in the photolysis of formic acid at 212.6 nm to be 300 ± 50 K. Our REMPI probe might be suited to studies that require both sensitive detection of the OH radical combined with accurate kinetic energy information.

Introduction

The important role the OH molecule plays in chemistry and physics and the interesting photoionization[1−3] and photodissociation dynamics[4] of its excited states have inspired the achievement of a number of laser-induced ionization schemes. In independent studies published at approximately the same time, ionization of the OH radical via two-photon-[5,6] and three-photon-resonant[7] excitation of the lowest lying Rydberg state ($D^2\Sigma^-$) was demonstrated. Ionization of the OH radical via two-photon resonant excitation of a newly observed $3^2\Sigma^-$ state was also demonstrated.[6] Finally, direct photoionization[8] and pulsed-field ionization of one-photon excited high lying Rydberg states[9] also was achieved. In comparison to laser induced fluorescence (LIF), these ionization schemes offer greater collection efficiency, mass discrimination, and improved sensitivity to translational energy. Despite their promise however, only a few subsequent studies[10,11] employed REMPI detection of OH radicals. The preferred detection technique has remained the A-state-LIF scheme introduced 20 years ago by Ondrey and co-workers.[12] We speculate that REMPI schemes for the detection of OH have not become more prevalent because of the intensity of UV radiation that must be employed to drive the $X^2\Sigma^- \rightarrow D^2\Sigma^-$ or $X^2\Sigma^- \rightarrow 3^2\Sigma^-$ transition with two- or three-photons. Under many experimental conditions, the tightly focused UV laser radiation required may lead to an intolerably large background due to nonresonant ionization processes. The one photon Rydberg state pulsed field ionization technique employing 95 nm radiation[9] was accomplished to study the dynamics of the Rydberg molecule rather than for sensitive detection. Because of the relatively weak available sources of v-UV laser radiation and the small oscillator strengths for ground-state to Rydberg-state transitions, it is unlikely that one-photon ionization will be developed as a sensitive method for detection of OH radicals.

In this paper, we investigate a new laser-induced ionization scheme that does not require an intense source of UV laser radiation. Specifically, we have ionized OH radicals produced in the photodissociation of formic acid via resonant excitation through the $D^2\Sigma^-$ state, as shown below:

$$HCOOH + h\nu(212.6\ nm) \rightarrow OH \quad (1)$$

$$OH(X^2\Pi_i) + h\nu(122.0-122.5\ nm) \rightarrow OH(D^2\Sigma^-) \quad (2)$$

$$OH(D^2\Sigma^-) + h\nu(440-430\ nm, 318.8\ nm) \rightarrow OH^*, OH^+(^3\Sigma^-) + e^- \quad (3)$$

$$OH^* + E(174\ V/cm) \rightarrow OH^+(^3\Sigma^-) + e^- \quad (4)$$

Here OH* is a high-*n* Rydberg state and the electric field *E* of eq 4 is provided by pulsing the bias voltage on a set of parallel plates that surround the excitation region.

In the next section, we describe the experimental apparatus. Results are given in the following section. These results include the rotational temperature of OH produced in the dissociation of formic acid at 212.6 nm, a correction to a published energy for the $6s^1\ 11p^1\ ^3P_1^0$ state of Hg, a new determination of the electronic energy T_0 of the D state of OH and an upper limit to the lifetime of the D state of OH.

Experimental Section

Lasers and Optics. Because our probe requires both tunable v-UV and UV laser radiation, the optical bench is somewhat involved. In total, 9 different wavelengths of laser radiation are employed (1064, ∼810, 637.5, 532, ∼430, 355, 318.8, 212.6, and ∼122 nm.) In addition to presenting a challenge for eye safety, the complexity of the optical bench required a great deal of time to optimize for maximum sensitivity. For this reason, the complete optical bench is illustrated in Figures 1 and 2 and described in detail here. Only the most effective pump scheme attempted is shown. Some data presented were taken with a less efficient pump beam arrangement.

For the majority of studies presented here, a single Nd:YAG laser is used to pump three dye lasers (Figure 1). The Nd:YAG laser produces 10 ns pulses of laser radiation at a repetition rate of 10 Hz. The IR output of the laser is typically 800 mJ and is frequency doubled to produce 300 mJ of 532 nm radiation. A dichroic mirror splits this 532 nm into beams of 200 mJ and 100 mJ per pulse. The 200 mJ pulse pumps a Lambda Physik Scanmate IIe dye laser to produce 50 mJ/pulse of laser radiation at 637.5 nm. This red laser radiation is frequency tripled using two BBO crystals[13] to produce 1.0

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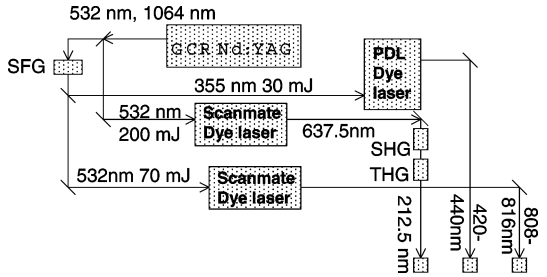

Figure 1. Optical bench used to create laser radiation required for the 1+1 REMPI scheme presented in this work.

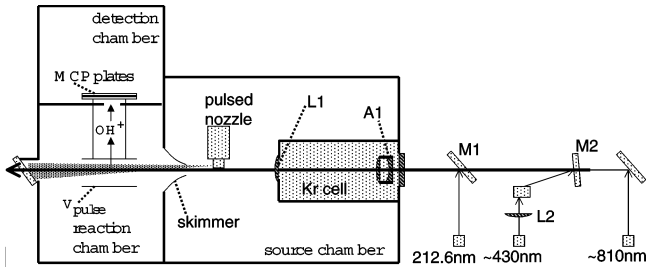

Figure 2. Experimental apparatus.

mJ/pulse of laser radiation at a wavelength $2\pi c/\omega_1 = 212.6$ nm. The 100 mJ pulse of 532 nm laser radiation is mixed with the fundamental of the Nd:YAG laser to produce 30 mJ of 355 nm laser radiation. The residual 532 nm laser radiation from this process (approximately 70 mJ/pulse) is used to pump a second Lambda Physik Scanmate IIe dye laser that produces 7 mJ of laser radiation tunable from $2\pi c/\omega_2 = 808$ nm to 816 nm. The required v-UV light at ~122 nm (eq 2) is obtained by resonant $2\omega_1 - \omega_2$ four wave mixing[14] in a pure gas of Kr. The 355 nm laser radiation is used to pump a third dye laser (Spectra Physics PDL II). This third dye laser produces 2.5 mJ of 420−440 nm laser radiation and allows us to investigate Rydberg states of OH excited from the $D^2\Sigma^-$ state and ionized by a pulsed electric field. We found that direct ionization can also be achieved with the 318.8 nm second harmonic of the 637.5 nm dye laser, simplifying the optical bench considerably. We note that to achieve effective ionization the residual 318.8 nm laser radiation is separated from the 212.6 nm laser radiation so that it may be focused in the probe region of the reaction chamber.

All required laser frequencies enter our vacuum chamber along a single axis, as shown schematically in Figure 2. A dichroic mirror (M1) is used to combine the IR laser radiation with the 212.6 nm UV laser radiation. This UV and IR laser radiation is focused into a mixing cell with a $f = 180$ mm achromatic lens constructed from a plano-concave fused silica lens and a plano convex MgF_2 lens. This focal point is inside a cell that contains pure Kr gas between 4.0 and 10 Torr, as measured with a Baratron gauge. The resultant $2\omega_1 - \omega_2$ radiation produced by four-wave mixing is focused into a probe chamber with a MgF_2 convex lens (L1, radius of curvature 60 mm). This lens is placed a distance of 300 mm away from the achromatic lens and both focuses the v-UV laser radiation into the probe region and isolates the Kr cell from the vacuum region. The diameter of the v-UV radiation in the probe region is measured to be 0.75 mm by using a vacuum feed through to translate a razor blade across the beam while monitoring the photoionization of pyridine by the v-UV laser radiation. Pyridine is chosen because it is readily ionized by v-UV laser radiation but does not show a strong two-photon ionization rate by the 212.6 nm laser.[15]

The blue light (420−440 nm) that promotes the $D^2\Sigma^-$ state to either a high lying Rydberg state or to $OH^+ + e^-$ is combined with the 212.6 and ~810 nm laser radiation with a dichroic mirror (M2). A fused silica lens (L2, radius of curvature 306 mm) is placed just before this dichroic mirror and 380 mm before the achromatic lens. This causes the ~420 nm light to be converging upon reaching the achromatic lens. For this reason, the focal point of the blue light occurs before the region at which v-UV light is generated and does not affect the four-wave mixing. In addition, this choice of focal point causes L1 to focus the ~420 nm radiation at approximately the same point that the v-UV laser radiation is focused, greatly increasing the ionization efficiency. The diameter of the blue light in the probe region is measured to be approximately 1.5 mm.

Vacuum Apparatus and Detection. The vacuum apparatus is shown schematically in Figure 2. It consists of a source chamber that produces a pulsed beam of formic acid seeded in He, a reaction chamber and a detection chamber. A molecular beam of formic acid seeded in helium is created in the source chamber. This beam enters the reaction chamber where the 212.6 nm laser radiation photolyzes the formic acid. The OH product of this dissociation is then ionized. A standard linear time-of-flight detector shown schematically in Figure 2 and described in detail elsewhere[16] is used to detect the OH^+ ion. The laser ionization typically occurs in the absence of an externally applied electric field. The ions are then accelerated by a 174 V/cm field by applying a 500-volt pulse to a set of extraction plates. This field pushes the ions through a field-free drift tube and on to a microchannel plate detector.

Results

Spectra of OH from the Photodissociation of HCOOH at 212.6 nm. The observed spectra of the 0−0 band of the $X \rightarrow D$ transition of OH molecules produced from the photolysis of HCOOH at 212.6 nm is shown in Figure 3. The spectral simulation is generated using a standard software package.[17] We use the rotational constants determined by de Beer and co-workers[6] and adjust the rotational temperature T_R and electronic energy T_0. By fitting the relative observed intensities of the $N'' = 1$, 2, and 3 lines of the Q1 branch, we find the rotational temperature to be 300 ± 50 K. This is consistent with the rotational temperature found at similar dissociation energies by de Beer et al.[6] and Singleton et al.,[8] but not Ebata et al.,[19] who observed $T_R = 680$ K at a dissociation wavelength of 225 nm.

This work does not resolve the discrepancy in the literature but instead offers some clues. The work of de Beer et al. employs a 2 + 1 REMPI probe via the D state, whereas both the work of Singleton et al. and Ebata et al. employ a 308-nm-LIF probe via the A state. The Singleton work employs dissociation radiation at 222 nm, a wavelength close enough to that used by Ebata et al. that a strongly wavelength-dependent final rotational temperature is an unlikely explanation. In addition, both Singleton et al. and Ebata et al. employed room-temperature samples, eliminating the possibility that T_R is greater in the Ebata experiment because of hot-band dissociation. In a previous experiment, we also employed a vapor cell to observe the OH product from the photodissociation of formic acid at 212.8 nm (the fifth harmonic of our Nd:YAG laser) using LIF fluorescence via the *A* state. The analysis of our spectra found a rotational temperature of ~700 ± 50 K, consistent the work by Ebata et al. Because of the wide variety of experimental conditions that lead to the ~300 K rotational distribution and the similarity between the two measurements that lead to the ~700 K distribution, our current hypothesis is that the lower

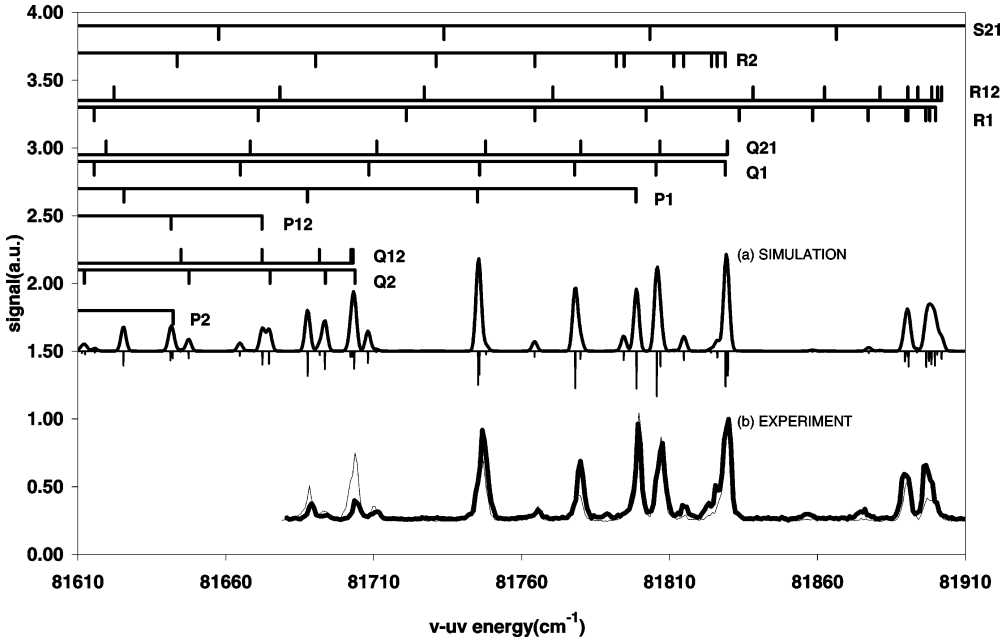

Figure 3. Spectrum of the 0−0 band of the $X^2\Pi \rightarrow D^2\Sigma^-$ transition of OH molecules produced from the dissociation of formic acid at 212.6 nm. (a) Top spectrum: simulation assuming $T_R = 300$ K with $\Delta\lambda = 0.005$ nm. (b) Experimental data with 430.8 nm ionization (thin line) and 318.8 nm ionization (thick line.)

temperature is the result of one-photon dissociation. We further speculate that either a multiphoton process involving 308 nm radiation or secondary collisions of the direct photoproducts can increase the measured value of T_R.

Determination of T_0 of the $D^2\Sigma^-$ State of OH and the Energy Level of the $6s^1 11p^1\ ^3P_1$ state of Hg. The value of the energy of the ground vibrational state of the $D^2\Sigma^-$ state is determined by Douglas,[20] Collard et al.,[5] and de Beer et al.[6] to be $T_0 = 81\,797.95$, $81\,795.8 \pm 0.5$, and $81\,815.8$ cm^{-1}, respectively. It should be noted that, in the text of the de Beer paper, good agreement is claimed to occur with the Douglas work. This may imply that de Beer et al. use an unconventional definition of the zero-point energy. We adopt the convention of Douglas and Collard et al. and define T_0 to be the energy splitting between the lowest energy state of the OH molecule and the lowest lying ro-vibrational level of the $D^2\Sigma^-$ state. To the resolution of our instrument (ignoring the lambda-doublet splitting of the ground state) T_0 corresponds to the energy of the P1, $N'' = 1$ transition. To determine which of the three reported values for T_0 is correct, we calibrated our laser by observing $1 + 1$ resonance enhanced ionization of Hg via the $6s^2\ ^1S \rightarrow 6s^1 11p^1\ ^3P_1{}^0$ and $6s^2\ ^1S \rightarrow 6s^1 11p^1\ ^1P_1{}^0$ transitions. The energy difference we observed between these two transitions does not match the difference expected from Moore's table of energy levels.[2] With our measured interval and the MIT wavelength tables,[22] we were able to trace the disagreement to a mistaken value for the $6s^1 11p^1\ ^3P_1{}^0$ energy level, which should be 81 807.6 cm^{-1}. (The Moore value is 81 811.876 cm^{-1}.) After calibrating our lasers, we determined that $T_0 = 81\,799 \pm 1$ cm^{-1}, in agreement with the original value given by Douglas.

Lifetime of the $D^2\Sigma^-$ State of the OH Molecule. From the line widths of their observed $2 + 1$ REMPI spectra, de Beer et al.[6] estimate a lower limit to the lifetime of the D state to be $\tau_{min} = 500\ (J'(J' + 1))$ps. To determine an upper limit to this lifetime, we employed a second Nd:YAG laser to pump the PDL dye laser tuned to 430.9 nm. This allowed us to vary the time between excitation of the $D^2\Sigma^-$ state and the ionization step. The D state was excited on three different transitions of the 0−0 band (Q1 branch, $N'' = 1$ and 2, and P1 branch $N'' = 1$.) For each of these three cases, simultaneous excitation of the D state and ionization was required. From this we can conclude that there is an upper limit $\tau_{max} = 8$ ns corresponding to the pulse duration of our Nd:YAG lasers.

Conclusions

Here we have demonstrated a $1 + 1$ REMPI scheme to detect the OH molecule that may be advantageous over LIF techniques under some circumstances. We have measured the rotational temperature $T_R = 300 \pm 50$ K of OH produced in the photolysis of formic acid at 212.6 nm. We have found a value for T_0 of the $D^2\Sigma^-$ state that is in agreement with a 1974 publication,[20] but not with other reported values.[5,6] We present a new value for the energy level of the $6s^1 11p^1\ ^3P_1{}^0$ state of Hg (81 807.6 cm^{-1}.) We have measured a 8 ns upper limit to the lifetime of the $D^2\Sigma^-$ state.

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