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Effect of collisions on one-color polarization spectroscopy of OH $A^2\Sigma^+ - X^2\Pi$

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The effect of collisions on the magnitude of polarization spectroscopy (PS) signals from the OH radical on the $A^2\Sigma^+ - X^2\Pi$ (0,0) band has been studied. OH was produced by the 266-nm photolysis of H₂O₂ and detected by one-color degenerate PS, using \approx 5-ns pulses from a Nd:YAG pumped dye laser. Spectra with both circular and linear pump polarizations are reported, together with signal dependence on OH number density and pump pulse fluence. The relative line intensities in the spectra and measured square dependence on OH number density are consistent with a description of PS as a variant of four-wave mixing spectroscopy. The pump pulse fluence dependence is fitted well by literature saturation curves. The collisional dependence of the PS signal was investigated by adding increasing pressures of He, Ar, or N₂ collider gases for fixed overlapping pump and probe pulses. The principal finding is the very rapid loss of the PS signal with increasing collider pressure. The resulting phenomenological rate constants are in the range 5–9 $\times 10^{-9}$ cm³ s⁻¹. We discuss these rate constants with reference to the literature rotational energy transfer and dephasing rate constants. We propose that the very large observed values may be explained by the effect of elastic velocity changing collisions. © 2003 American Institute of *Physics.* [DOI: 10.1063/1.1615515]

I. INTRODUCTION

A. General background

It is a very-well-established fact that molecules may be collisionally removed from electronically excited states. Total rate constants for this "quenching" have been measured on numerous occasions. However, the fate of the quenched molecules has been little studied. Dagdigian recently reviewed the current state of the field for the simplest molecular systems: diatomic molecules.¹ Rotational- or vibrational-state product distributions have been measured for only a limited range of molecular species, with state-to-state relative rate constants being the most detailed level of information obtained. A quantitative theoretical understanding of these processes is still lacking, and simple models of energy disposal have been shown to have generally poor predictive ability.²

In the more developed field of study of reactive collisions, the vector properties (for example, rotational angular momentum polarization) of the process have been shown to be a sensitive probe of the forces between the molecules.³ For inelastic collisions such properties have also been measured, but to a much more limited extent. They have given new insights into the nature of the collisional interactions, notably in the very detailed recent work on NO/Ar rotational energy transfer (RET) collisions by Cline and co-workers.^{4,5} These studies measured state-to-state differential cross sections and scattering angle-resolved product angular momentum polarization. Angular momentum polarization in electronic energy transfer has not received the same level of attention. Among the very few studies that have been reported, Jackson *et al.*⁶ measured polarization retention in inelastic electronic energy transfer in the SiF radical. These experiments were performed using dispersed fluorescence to detect the collisionally transferred population. The method involved resolving the polarization of the emitted fluorescence with a photoelastic modulator and polarizer combination. These experiments proved extremely challenging within the practical signal-to-noise limits provided by dispersed fluorescence.

We have recently extended our studies of electronic energy transfer to the *A* and *B* states of the CH radical with a range of colliders.^{7,8} This has been shown to be a rapid process with a variety of partners, and vibrationally resolved branching ratios have been established. The rotational distribution of the transferred CH has been resolved using one of the more efficient partners: CO_2 (Ref. 9). However, the signal-to-noise limits of dispersed fluorescence again prevent the practical extension of this work to polarization studies of the CH system.

CH, typical of many other systems, does not happen to provide any suitable higher-lying electronic states through which to perform an alternative optical–optical double-resonance experiment—for example, by laser-induced fluo-rescence (LIF)—as has been reported for some other limited classes of molecules.^{10,11} We have therefore been trying to develop a method of measuring the influence of collisions on the angular momentum polarization of electronically excited species.

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The spectroscopic technique we are using is polarization spectroscopy (PS). Wieman and Hänsch first developed polarization spectroscopy as a variant of saturation spectroscopy.¹² In the simplest implementation of PS the output of a single tunable laser is split into two beams. The first of these, the pump beam, is either circularly or linearly polarized. The second, the probe beam, is linearly polarized before passing through the sample (at a 45° angle to the pump beam polarization if that is also linearly polarized), after which it encounters a blocking crossed polarizer. The pump and probe beams are overlapped in the sample, in either a copropagating or counterpropagating geometry. When the pump beam is resonant with a transition in the sample it can be considered to produce a polarization-dependent saturation. The probe beam "sees" the sample as birefringent, and consequently the polarization of the transmitted probe beam becomes slightly elliptical, with a change in principal axis. The resulting component of the probe beam normal to the initial polarization then leaks through the crossed analyzing polarizer and may be detected, typically by a photomultiplier tube.

In recent years PS has undergone something of a revival and has been widely applied in combustion diagnostics as a tool to detect radical species, notably OH,^{13,14} NH,¹⁵ C₂,¹⁶ and NO.¹⁷ These applications are all of degenerate PS, in which a single laser is used to generate both pump and probe beams. Infrared-ultraviolet double-resonance polarization spectroscopy of OH and CH3 has also very recently been demonstrated.¹⁸ A number of experiments have been devoted to studying the collisional evolution of the signal as a function of the delay time between pump and probe pulses. The majority of these studies have been performed in atmospheric pressure flames, using picosecond lasers and optical delay lines.^{19,20} Only a single study has been performed in a controlled temperature and pressure environment containing a single collider species, without variation of the pumpprobe delay time.²¹ In related work, Wilson and McCaffery have used continuous-wave lasers in a double-resonance PS experiment to measure line shapes and hence infer details of the differential scattering cross sections.²²

B. OH collisional energy transfer

We have chosen the OH radical as a test case for our initial development of our experiments as it is simple to produce and probe. Collisions of this radical have been the subject of numerous previous experimental studies in both the ground $X^2\Pi$ and excited $A^2\Sigma^+$ states, primarily because of its importance in combustion and the atmosphere. There have been several recent studies of the ground $X^2\Pi$ state. Kliner and Farrow²³ measured the evolution of the nascent rotational-state distribution produced by the 266-nm photolysis of H₂O₂ using picosecond LIF. The rotational-state distributions at different photolysis-probe delays were recorded and a variety of collisional models were used to simulate them. Several different colliders were used—H₂O, Ar, N₂, and O₂—and the data were well fitted by an exponential gap law model. Most relevant for the current work were the reported total depopulation rate constants. These span the range from 2×10^{-10} cm³ s⁻¹ for Ar through to 8.9×10^{-10} cm³ s⁻¹ for H₂O. This included an assumed contribution of 4.5×10^{-10} cm³ s⁻¹ to account for the unmeasured Λ -doublet changing collisions. These rate constants were for the lowest five or so rotational levels and were essentially invariant with *N*".

A more sophisticated experiment has been performed by Hickson *et al.*^{24,25} OH $X^{2}\Pi$ was produced by photolysis of HNO₃ at 266 nm. A single Λ -doublet selected rotational level was prepared in the OH v''=1 vibrational level, using a pulsed tunable infrared laser. The evolution of the resulting population in the prepared state and its transfer into other rotational levels was then monitored by LIF on the A-Xband. The Λ -doublet changing collision rates were found to depend strongly on the identity of the collider. The transfer rate constant for J=3.5 with HNO₃ was found to be 2.4 $\times 10^{-9}$ cm³ s⁻¹, while that for Ar was only 0.5×10^{-10} cm³ s⁻¹. Total removal rate constants excluding Λ -doublet transfer ranged from 1.0×10^{-10} cm³ s⁻¹ for Ar to 5.0 $\times 10^{-10}$ cm³ s⁻¹ for HNO₃.

These two studies quote rotational energy transfer rate constants for OH $X^2\Pi$ that agree well with older literature and show that the process is very rapid with H₂O and HNO₃. Measurements by Andersen *et al.*²⁶ indicate that H₂O₂ is also very efficient, with total rate constants of the order of $1-10 \times 10^{-10}$ cm³ s⁻¹.

Both electronic quenching of the $A^{2}\Sigma^{+}$ state and RET within it have been studied on numerous occasions. Jorg *et al.*^{27,28} have measured RET rate constants for OH $A^{2}\Sigma^{+}$ (v'=0) with a variety of combustion-related collision partners and rare gases. These experiments were performed by dispersed fluorescence measurements after pumping of single rotational levels in the $A^{2}\Sigma^{+}$ state. With H₂O as a collision partner, individual state-to-state rate constants of up to 4×10^{-10} cm³ s⁻¹ were measured, with a total removal rate constant of approximately 9×10^{-10} cm³ s⁻¹. N₂ gave individual rate constant of approximately 5×10^{-10} cm³ s⁻¹, while total removal rate constants for Ar and He were 2.5 $\times 10^{-10}$ and 7.5×10^{-11} cm³ s⁻¹, respectively.

The majority of the collision partners discussed here show $A^{2}\Sigma^{+}$ state electronic quenching rates which are much slower than the RET rates. N₂ has typical rotational-level-dependent quenching rate constants of $k_{Q}=2\times10^{-11}$ cm³ s⁻¹, while He and Ar have quenching rates that are negligible.^{29,30} H₂O, on the other hand, has a very large quenching rate constant $k_{Q}\approx7\times10^{-10}$ cm³ s⁻¹, effectively independent of rotational level.^{31,32}

In this paper, we present phenomenological rate constants for the collisional suppression of PS signals of OH (A-X). PS was performed in a degenerate (pump and probe beams from the same laser) copropagating configuration. We investigate the pump power, OH number density, and collider pressure dependences of the PS signal. Pump power and number density dependences are discussed in light of previously published theory. The principal new result, the effect of collisions on the PS signal, is discussed in the context of other literature OH collisional rate constants.



FIG. 1. Schematic of the experimental apparatus used for one color polarization spectroscopy. WP=waveplate, DFR=double Fresnel rhomb, BC =Berek's compensator, SF=spatial filter, PMT=photomultiplier tube, and M=Molectron energy meter.

II. EXPERIMENT

The experimental apparatus is shown in Fig. 1. Experiments were conducted in a glass flow cell (50 cm long, 5 cm diameter), evacuated by a rotary pump. The cell had windows (UV, synthetic fused silica) at each end and one on the side for LIF detection. Hydrogen peroxide (50% wt/H₂O) was introduced by bubbling the selected quenching gas through the solution and the pressure regulated by a needle valve; additional quencher was added downstream when required through a secondary needle valve. All of the piping and valves after the bubbler were made of Teflon to reduce dissociation of the hydrogen peroxide. The hydrogen peroxide was photodissociated using the fourth-harmonic output of a Nd:YAG laser (Continuum Surelite II-10) at 266 nm, producing OH $X^{2}\Pi$ radicals. A Nd:YAG pumped dye laser (Continuum Surelite II-10, Sirah Cobrastretch, nominal pulse length 5 ns, R640 dye) provided tunable narrow-band radiation in the 308-nm range, resonant with the OH A - X(0,0)band. A delay of 8 μ s, controlled by an electronic delay generator (SRS DG535), was introduced between the firing of the two laser systems to allow relaxation of the nascent OH to thermal Boltzmann rotational and translational distributions.

A central portion of the dye laser output, ≈ 2 mm in diameter, was selected by an iris and used in the subsequent experiments. All beam steering was carried out using broadband dielectric mirrors (Balzers). The beam was split into two parts using a tunable waveplate and a calcite polarizer. The weaker of these beams (the probe beam) was passed to a high quality polarizer (Bernard-Halle, extinction ratio $< 1 \times 10^{-6}$) mounted in a precision rotation stage (Newport). The probe beam passed directly through the cell without encountering any additional optics other than the cell windows. The more intense beam (henceforth the pump beam) was passed through a double Fresnel rhomb and calcite polarizer combination, which acted as a variable attenuator. The pump beam was passed through a Berek's compensator (New Focus) to produce light that could be selected as either circularly polarized or linearly polarized at a 45° angle to the polarization of probe beam. The pump beam was then overlapped with the probe by positioning a final turning mirror so that the probe beam just passed its edge. This ensured that the overlap length was as long as possible. Both beams overlapped the photolysis beam (counterpropagating to the pump and probe beams) in the center of the cell. At the exit of the cell the pump beam was picked off by another mirror and passed to an energy monitor (Molectron). The probe beam passed through an iris and then a second, identical highquality polarizer, mounted in a precision rotation stage (Bernard Halle/Newport). This polarizer was crossed with respect to the first. The signal beam that emerged from this analyzing polarizer was passed by a number of mirrors around the optical table a distance of approximately 2.5 m to a spatial filter and then through a 308-nm centered interference filter to a photomultiplier tube (PMT), which was carefully shielded from the ambient light.

A second PMT collected LIF from the central portion of the cell. No collection optics was used. In fact, it was necessary to attenuate the fluorescence using neutral density filters to avoid saturation of the PMT. Signals from both PMTs and the energy monitor were passed to boxcar averagers (SRS) and thence to a computer on a shot-to-shot basis. The computer also controlled the wavelength scanning of the dye laser via purpose-written Labview software.

A significant limitation in the application of PS in sealed environments arises from stress-induced birefringence in the windows of the cell. The birefringence causes the polarization of the probe beam to become elliptical, resulting in a constant background signal passing through the analyzing polarizer, independent of whether the probe beam is resonant with a transition in the sample. In these experiments, it was found that applying a compensating stress to the cell was capable of nulling any stress-induced birefringence to acceptable levels. The birefringence of the windows was minimized before each experiment, and checked at regular intervals.

III. THEORY

Polarization spectroscopy is a specialized form of fourwave mixing (FWM).³³ Like FWM, in the perturbative lowpower limit the signal depends on the square of the pump beam fluence and linearly on the probe beam. Similarly, the signal depends on the square of the number density of the probed species and quartically on the line strength of the transition used.³⁴ Beyond the perturbative treatment, there have been a number of papers treating the strong-field limit using numerical simulations.^{35,36} Crucial to this study, the signal also depends on the collisional processes of both the ground and excited states linked by the probed transition. Collisions that involve pure dephasing as well as population transfer out of, or between, the m_1 sublevels of the two resonant states are significant. This results in a dependence on both pure rotational population transfer and orientation or alignment loss.

The detailed contributions of these different processes will be addressed fully in future reports. In this paper, we restrict ourselves to degenerate one-color experiments and assume a single phenomenological collisional decay rate containing contributions from both the ground and excited states.



FIG. 2. Part of the OH $A^2\Sigma^+ - X^2\Pi$ (0,0) band with partial assignment. (a) Polarization spectroscopy with 45° linearly polarized pump light of rotationally thermalized OH. (b) Polarization spectroscopy with circularly polarized pump light of rotationally thermalized OH. (c) LIFBASE simulation of LIF spectrum produced by a 300-K Boltzmann distribution. Spectra recorded with 2 Torr of Ar buffer and 8- μ s photolysis/PS delay under slightly saturating pump fluence conditions.

IV. RESULTS

A. Spectra

Figure 2 shows three spectra of the OH $A^{2}\Sigma^{+}-X^{2}\Pi$ (0,0) transition for comparison: (a) PS with linearly polarized

pump light at 45° to the probe polarization, (b) PS with circularly polarized pump light, and finally (c) LIF simulation (LIFBASE).³⁷ The PS spectra were taken under slightly saturating pump laser conditions. Very clear differences are apparent between all three pairs of spectra. It is immediately obvious that neither PS spectrum resembles the LIF spectrum with respect to line intensities. The linearly polarized pump PS spectrum predominately features Q-branch lines, while in the circularly polarized pump spectrum P- and *R*-branch lines are most intense. These observations are, as expected, consistent with previous descriptions of PS.^{13,15,17} Orientation is not an efficient process with circularly polarized light via Q-branch transitions and becomes increasingly difficult with increasing rotational quantum number. This explains the strong preference for P and R branches in Fig. 2(b). Alignment with linearly polarized light is stronger via Q-branch transitions than P/R. Additionally, analogous with degenerate four wave mixing (DFWM), we expect the PS signal to depend on the line strength of the transition to the fourth power, which will strongly favor the Q branch over Por R, as seen in Fig. 2(a). In both PS spectra, the signal intensity drops off much more rapidly with increasing rotation than in the LIF spectrum. This is also consistent with a DFWM description, from which we expect the signal to depend on the square of the number density of the probed species, as quantified in the next section.

B. Number density dependence of signals

The number density dependence of the PS signal was determined by varying the OH concentration via the photolysis fluence. As an example, the probe laser wavelength was centered on the $P_1(1)$ line and the signal-to-noise optimized at maximum photolysis fluence, as measured immediately before the cell using an energy meter (Scientech). Data were acquired in the form of averages of 100 laser shots. The fluence was then reduced by altering the photolysis laser flashlamp voltage and the measurement repeated. The measurements were made over the full range of available fluences. The polarization spectroscopy data were corrected for minor variations in probe laser system fluence (see next section). The results are shown in Fig. 3, and the PS signal clearly follows a nonlinear dependence on the OH number density. This shows good agreement with the expected $[OH]^2$ -dependent curve also shown in Fig. 3.

C. Effect of pump laser fluence

The pump beam fluence was varied by adjusting the tunable waveplate prior to the second calcite polarizer; this allows independent control of the pump and probe fluences. The PS signal and pump fluence after the cell were averaged over 50 shots: then, the pump fluence was altered and the process repeated. The pump fluence was varied over the desired range several times during a single experiment to ensure against other possible systematic experimental variations. A number of different transitions were studied, with both linear and circular pump polarizations. All of the spectra show similar functional forms, with clear evidence of saturation at the higher fluences.



FIG. 3. Polarization spectroscopy signal as a function of OH number density. Open circles are experimental data; the solid line is a $[OH]^2$ simulation.

Walewski *et al.* recently published a paper on the effect of pump fluence on polarization spectroscopy signals.³⁸ They listed several functional forms for the expected dependence, drawing on simple descriptions of the saturation dependence of DFWM experiments, including

$$I_{\rm PS} = A \left(\frac{I_{\rm pump}}{I_{\rm pump} + I_{\rm sat}^{\rm PS}} \right)^2,\tag{1}$$

where I_{PS} is the measured signal, I_{pump} is the pump laser intensity, A is an arbitrary scaling factor, and I_{sat}^{PS} is a saturation intensity.

An example of the fit of Eq. (1) to the data for linear polarization on the $P_1(1)$ line is shown in Fig. 4. It can be seen that the functional form fits the data well. The signal



FIG. 4. Polarization spectroscopy signal as a function of pump laser fluence. Open circles are experimental data; the solid line is a fit of equation 1 to the data. Inset diagram shows an expanded view of the low-fluence region.

dependence at low fluence is shown in the inset diagram. It is observed that the signal follows a squared dependence at the lowest pump fluence. All further experiments were performed in this low-power regime.

D. Effect of varying collider pressure

The primary aim of this wider program of experiments is to study inelastic collisional processes using polarization spectroscopy. This first stage is aimed at establishing the evolution of the PS signals with increasing collision number. Varying the time between the pump and probe pulses at constant pressure would clearly be a straightforward way of achieving this. However, in the current one-color degenerate experiment this can only be realized by introducing an optical delay line, and while this has been used in several picosecond PS studies, the path lengths required are clearly not practical in this nanosecond experiment.

The alternative approach of varying the collider pressure at fixed pump-probe delay was thus applied. The laser wavelength was centered on the selected transition with the pump and probe beams essentially coincident in time through having traversed beam paths of equal length. The PS signal was then acquired for 100 shots, along with the shotto-shot pulse energy of the pump beam and LIF signal. The pressure of the selected collider gas was then altered and the procedure repeated. The LIF signal was acquired to allow normalization of the PS signal to the number density of OH produced by photolysis. Several difficulties presented themselves. The concentration of H₂O₂ required to produce sufficient signal-to-noise was high enough that significant quenching of the OH A $^{2}\Sigma^{+}$ fluorescence was observed. This is a side effect of the relatively modest photodissociation cross section of H_2O_2 at 266 nm $[5 \times 10^{-20} \text{ cm}^2 \text{ (Ref. 39)}]$. The addition of extra collider gas was found to alter the flow rate of H₂O₂, which could not be controlled using a mass flow controller due to the rapid dissociation of the H_2O_2 on stainless steel surfaces. Both the OH concentration and quenching of the OH A ${}^{2}\Sigma^{+}$ fluorescence were affected by the selected pressure of the collider gas. The integrated OH LIF signal over a fixed time gate was thus not a simple direct measure of the OH concentration.

Therefore, the LIF decay trace was acquired using a digital storage oscilloscope (LeCroy 3900) at each pressure point. The resulting exponential lifetime from a fit to this decay trace was used together with the known collision free fluorescence lifetime of OH A $^{2}\Sigma^{+}$ to correct the LIF signal for the effects of quenching. The hypothetical magnitude of the LIF signal without quenching was established at each pressure. The square of this value was then used to normalize the measured PS signal with respect to OH concentration. The PS signal was also normalized with respect to the dye laser fluence. This should be a squared dependence on the pump power and linearly on the probe fluence or cubic in the total. However, the LIF signal is itself linear in the laser fluence, and dividing by the square of the LIF signal has already introduced a partial normalization for variations in laser fluence. The PS signal was accordingly divided linearly by the laser fluence, resulting in the correct overall normalization.

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FIG. 5. Polarization spectroscopy signal as a function of Ar collider pressure, for the $P_1(1)$ transition with circularly polarized pump light. Open circles are experimental data: the solid line is a first-order exponential fit to the data.

The total pressure of precursor and collider was varied over a range of ≈ 0.5 to ≈ 5 Torr. At the lowest total pressures the observed LIF lifetime indicated that the H₂O₂ precursor partial pressure was ≈80 mTorr, falling to <10 mTorr at the highest total pressures. The colliders used were He, Ar, and N2. Additionally, O2, CO2, and H2 were also tried, but produced such rapid quenching of the LIF that normalization to the varying OH concentration became unreliable. For each of the collider gases used, both circular and linear polarizations of the pump laser were applied. For the linearly polarized pump experiments the measured transitions were $P_1(1)$, $Q_1(2)$, and $Q_1(3)$ and for the circularly polarized pump the $P_1(1)$ and $P_1(3)$. First-order exponential decays were nonlinear least-squares fitted to the resulting curves of PS signal versus total pressure (collider $+H_2O_2/H_2O$). An example decay trace and fit are shown in Fig. 5. The resulting decay constants were converted to second-order rate constants by assuming a time scale of 5 ns, consistent with the manufacturer-quoted full width at half maximum (FWHM) pulse width of the Continuum/Sirah laser system. The rate constants derived for the three gases with both pump polarizations using the above transitions are listed in Table I. The

TABLE I. Phenomenological rate constants of PS signal loss [k (10⁻⁹ cm³ molecule⁻¹ s⁻¹)] as a function of pump polarization, collider gas, and transition probed. Errors quoted are 2σ statistical uncertainties.

	Linear pump polarization collider			Circular pump polarization collider		
Transition	He	Ar	N ₂	 He	Ar	N_2
$P_{1}(1)$	5.4±1.2	8.8 ± 0.8	6.2±1.0	8.0 ± 1.6	8.0 ± 0.4	7.6±0.8
$P_{1}(3)$	-	-	-	$8.0\!\pm\!0.6$	8.2 ± 1.2	6.7 ± 0.6
$Q_1(2)$	$6.6\!\pm\!0.6$	$8.7\!\pm\!1.0$	$6.5\!\pm\!0.8$	-	-	-
$Q_1(3)$	5.3 ± 0.6	$8.6\!\pm\!1.0$	$8.3\!\pm\!1.0$	-	-	-

rate constants derived are not purely the result of collisions with the added collider gas, owing to the varying precursor partial pressure. However, the precursor partial pressure decreased as the collider pressure was increased, and we believe that the derived rate constants are hence primarily determined by the collider gas.

We have subsequently repeated a limited number of these measurements under different experimental conditions. These experiments were performed in a steel high-vacuum chamber, with OH radicals produced by the 193-nm photolysis of HNO₃. The much larger cross section for HNO₃ photo dissociation at this wavelength $[1.1 \times 10^{-17} \text{ cm}^{-2}]$ (Ref. 40)] resulted in excellent signal to noise with a partial pressure of only 10 mTorr of HNO₃ precursor. The different chamber and pumping and gas handling systems enabled the partial pressure of the precursor to be kept much more stable as the collider gas pressure was increased. The low HNO₃ partial pressure also resulted in no significant quenching of the OH LIF. As a result, the LIF signal was a much more direct measurement of the OH concentration, and a considerably less severe normalization of the PS signal was required compared to the results reported above. The pump and probe pulses were provided by separate lasers, the probe pulse by the same Nd:YAG/dye-laser combination as the one-color experiments and the pump pulse by a separate Nd:YAG/dye-laser system (Lumonics Hyperdye). The pump and probe pulses with synchronized temporally using a digital delay generator (SRS DG535). All other conditions were identical to the previous experiments. These later measurements also found extremely rapid phenomenological decay rates, confirming the results of the earlier measurements. This independent verification reinforces our confidence in the reported rate constants.

V. DISCUSSION

The measured signals have the anticipated dependence on laser pulse fluence and OH concentration from analogy with DFWM theory, with a squared dependence on the pump laser power and on OH number density. The strong variation of PS signal with transition branch seen in the spectra is consistent with a fourth-power line strength dependence. The squared number density dependence and low roomtemperature Boltzmann rotational populations, arising from the large rotational constant of OH, restrict us to only low N(<4) with a practical signal-to-noise ratio in these experiments.

The striking principal finding of these experiments is the extremely rapid removal of the polarization spectroscopy signal with increasing pressure. The rate constants quoted in Table I assuming a 5-ns pulse length are of the order $5-8 \times 10^{-9}$ cm³ s⁻¹. By analogy with DFWM, we should expect the signal detected to depend on the square of the electric field generated in the nonlinear process. The phenomenological rate constants will hence be twice the rate constants for the processes removing this signal electric field—for example, RET or reorienting collisions. Even so, the implied collisional rate constants of $2.5-4 \times 10^{-9}$ cm³ s⁻¹ are still extraordinarily fast. As discussed in the Introduction, total collisional removal rates for OH in the ground and excited

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states with Ar, N₂, or He as collision partners are at most of the order of 5×10^{-10} cm³ s⁻¹. We thus need to consider what other processes could be removing the signal in such a rapid fashion.

We can clearly state that whatever process removes the signal is collisional in nature. Polarization spectroscopy will be sensitive to purely elastic dephasing collisions as well as collisional removal or depolarization. The magnitude of these dephasing rates can be estimated from a combination of line broadening measurements, sensitive to both dephasing and total removal rates, and the literature total removal rates. The line broadening parameters for OH (A-X) with Ar, He, and N₂ are consistent with combined dephasing and removal rate constants of 5×10^{-10} , 2×10^{-10} , and 8×10^{-10} cm³ s⁻¹ respectively.⁴¹ These are very similar to the total collisional removal rate constants measured in other experiments and discussed earlier. This suggests that dephasing collisions are not a dominant influence on the observed degradation of our PS signal.

Further collisional processes that could potentially degrade the signal are those that result in a velocity change.⁴² The physical principle is that molecules that have undergone a velocity changing collision will emit spatially out of phase with their counterparts that have not, and the resulting interference will be destructive and not generate a signal field. The critical parameters are the wave vector for the signal field generated in the nonlinear process, the velocity change caused by collision, and the time scale between collisions and photon interactions. The wavelength of the pump and probe lasers is approximately 308 nm: from this, we find that the wave vector in these experiments is of the order $|\mathbf{k}| \approx 2 \times 10^7 \text{ m}^{-1}$. The most probable speed for OH at this temperature is \approx 540 m s⁻¹. The time scale of the experiment is ≈ 5 ns (the laser pulse length) during which three separate interactions (two with the pump beam and one with the probe beam) must occur for a signal to be generated. Consider two molecules with the same initial velocity, both interacting with the same beam, at the same instant. The first of these molecules undergoes no collisions until its next optical interaction. The other molecule undergoes an immediate elastic collision, which changes its velocity projection on the beam direction. After 5 ns it also undergoes its next optical interaction: however, it is now no longer in phase with its counterpart. The time between interactions and the change in velocity combine to result in a phase shift of $(\mathbf{k} \cdot \Delta \mathbf{v}) \Delta t$ between these formerly identical molecules. If we assume a time of 5 ns and the above wave vector, we find that a velocity shift of 31 ms⁻¹ is sufficient to generate a phase shift of π radians. This would result in the contributions to the signal electric field from these two molecules canceling one another. Thus relatively modest changes in velocity during the experimental time scale are sufficient to remove the PS signal. It should be emphasized that PS is sensitive to the velocity projection along the beam propagation direction. Collisions do not need to change the speed of the OH, which would require hard, repulsive wall interactions. Long-range, purely elastic interactions sampling the attractive part of the potential, which merely alter the direction of motion, would be sufficient. The representative 31-ms⁻¹ velocity shift estimated above would be produced by scattering through an angle of only $\approx 3^{\circ}$. Such small-angle scattering around the forward direction is known to typically have very large cross sections.⁴³ In the absence of further evidence, we propose that such velocity changing collisions are the primary process responsible for the loss of the signal in these experiments.

In conclusion, these experiments have been the first stage in a program to develop polarization spectroscopy as a probe of the dynamics of inelastic collisions. We have managed to produce high signal-to-noise PS signals in a sealed environment at low pressure, overcoming the problems of scattering pump light and birefringence introduced by the cell windows. The signals behave in the expected fashion with varying pump power or sample number density. The rate of loss of signal as a function of increasing collider pressure is unexpectedly extremely rapid, a process we attribute to predominately velocity changing collisions.

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