Collisional quenching of high rotational levels in $A\ ^2\Sigma^+$ OH

Brooke L. Hemming,[a] David R. Crosley,[b] Joel E. Harrington,[c] and Volker Sick[d]

Molecular Physics Laboratory, SRI International, Menlo Park, California 94025

Collisional removal of the $v'=0$ level of the $A\ ^2\Sigma^+$ state of the OH radical has been studied as a function of rotational level N' at room temperature. OH in high rotational levels of the $X\ ^2\Pi_i$ state were created by 193 nm photolysis of HNO_3 and excited to $A\ ^2\Sigma^+$ by a tunable dye laser. Time decays of fluorescence at varying pressures were measured. For O_2 and H_2, the quenching cross section σ_Q decreased with increasing N' until $N'\sim10$; for higher N' it appears to remain approximately constant. Xe behaves the same way except that the decrease continues to $N'=15$. For Kr, σ_Q appears to decrease to within experimental error of zero at $N'=10$; and for N_2 it was within error of zero above $N'=10$. These results have implications for laser-induced fluorescence atmospheric monitoring of OH and combustion temperature determinations, as well as a fundamental understanding of collisional quenching. Quenching of OH, $N'\sim1$, by HNO_3 was found to be $81\pm8\ \text{Å}^2$. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1386783]

INTRODUCTION

The collisional removal, or quenching, of the $A\ ^2\Sigma^+$ state of OH has been studied for over 40 years. However not until the early 1980s, when lasers could be used to excite single rotational levels N', was it was recognized that quenching in $v'=0$ depended on the value of N' that was quenched.[1,2] This followed a slightly earlier discovery[3] that vibrational energy transfer (VET), $v'=1\rightarrow0$ in the same electronic state also depended sharply on N'. These findings were explained in terms of an attractive, anisotropic potential surface between OH and the collision partner.[3,4] The fact that the surface is attractive is indicated by quenching cross sections σ_Q that are gas kinetic in size for many collision partners. This would then lead to a short-lived collision complex that could result in vibrational transfer (if in $v'=1$) or quenching. The anisotropy of the surface means that, at certain orientations between OH and the partner, the surface is more congenial to complex formation. For no rotation, these attractive valleys would be easy to enter. As the OH rotates faster and faster, it washes out the orientational influence, leading to a smaller likelihood of complex formation and thus a smaller σ_Q.

The NH radical was also found[5] to have σ_Q in its $A\ ^3\Pi_i$ state that were large and depended on N'; the reason was explained in the same way. It was conjectured[4] that for both radicals the N' dependence should disappear at very high rotational levels, where the rotational terminal velocity was as fast as the intermolecular approach velocity, so that the surface would appear isotropic to the collider. Thus yet higher N' would thus make no further difference in σ_Q. An experiment[6] designed to test quenching of high N' of NH was performed, producing high rotational levels in the ground state by 193 nm photolysis of NH_3 and exciting to the A state with laser induced fluorescence (LIF). For five different collision partner σ_Q first decreased with N' but then generally became constant for N' as high as 24.

In the present experiment we extend the study of N' dependent quenching in OH to high rotational levels. The experimental approach is very similar to that of Ref. 6, except that we use HNO_3 as the photolyzed precursor to OH in high N'' of the ground state. We do find an apparent leveling off of σ_Q for N' above 10 for three of the five colliders, but a decrease to nearly zero for Kr and N_2.

The results have implications for practical uses of LIF for atmospheric measurements of OH. One concerns the HO_x radical family. A LIF experiment is flown by Harvard University in the nose cone of the NASA ER-2 stratospheric aircraft to measure OH and HO_2 (the latter by chemical titration to OH which is the species actually detected).[7] In this experiment, the OH is excited to $v'=1$ and undergoes VET by the ambient air to $v'=0$, whose fluorescence is detected. Knowledge of vibrational transfer and quenching rates is needed to understand the fluorescence quantum yield Φ in these field experiments. Studies have been made of both quenching[8] and VET[9] for thermal distributions at temperatures between 300 and 200 K, indicative of the range sampled by the ER-2. However, it is also known that the VET process produces an incipient rotational distribution in $v'=0$ that populates higher N' than in a thermal distribution.[10] If rotational thermalization does not occur before quenching, this could affect the quantum yield. From the N' dependent σ_Q reported here, the range of this Φ could be calculated at room temperature. In the final paper in this series, we will report the temperature dependence of the N' dependence for temperatures below 300 K.[11]

A second application concerns a second instrument, also operated by Harvard University.[12] This Lyman-α hygrometer

[a]Also at: Chemistry Department, Stanford University. Present address: American Association for the Advancement of Science, Washington, DC.
[b]Electronic mail: drc@mplvax.sri.com
[c]Present address: Continuum, Santa Clara, California 95051.
[d]Visiting Fellow from University of Heidelberg. Present address: Department of Mechanical Engineering, University of Michigan, Ann Arbor, Michigan 49931.

is used to measure trace levels of H_2O vapor, as found in the upper troposphere and stratosphere. Ly-α radiation photolyzes H_2O, producing OH directly in the $A\,^2\Sigma^+$ state, which then fluoresces. The rotational distribution of the $v'=0$, $A\,^2\Sigma^+$ OH is at very high levels, as much as $N'=20$. Again, collisional quenching information for high N' is needed to interpret the quantum yield as a function of rotational level and collider.

These quantities are also important for calculation of Φ in other circumstances. For example, the rotational population distribution of OH in flames can be used as a precise flame thermometer.[13] To accomplish this in atmospheric pressure flames where collisions dominate the quantum yield, the N' dependent quenching must be known and incorporated.[14] The same is true for obtaining nonthermal rotational distributions in OH, for example in plasmas or as photolysis or reaction products, given that the pressure is high enough that quenching is important.

In addition to these applications, quenching of OH provides insight into fundamental collisional dynamics. The dependence of OH quenching on rotation likely owes its effect on the entrance channel to the collision. OH is small enough that for interaction with rare gases and H_2, at least, high quality *ab initio* surfaces can be calculated. This has been done for Ar[15] and He,[16] including the computation of state-specific rotational energy transfer cross sections in the $A\,^2\Sigma^+$ state via quantum scattering on these surfaces, collision complex formation leading to quenching could also be investigated. The conical intersection for N_2 interacting with the $A\,^2\Sigma^+$ and $X\,^2\Pi_i$ states has been computed and compared with van der Waals OH–N_2 studies.[17] The potential surfaces with OH interacting with H_2 show a conical intersection leading to both quenching and chemical reaction. For the purpose of an understanding of the quenching process in OH, we have included H_2, Kr, and Xe to our list of collision partners. For H_2, an N' dependence of σ_Q is known[2] for low N', and we study here its effect at high N'. Kr and Xe were found to have very large σ_Q, 8 and 27 Å^2, respectively, in a study of rotationally thermalized $A\,^2\Sigma^+$ OH at room temperature.[18] Thus for these rare gases, quenching will occur as fast or faster than rotational thermalization at high N', and can be expected to show an N' dependence if present.

EXPERIMENTAL APPROACH AND RESULTS

Photolysis of HNO_3 by a 193 nm layer produces OH in highly excited rotational levels of $v''=0$ in the $X\,^2\Pi_i$ state. In Ref. 19, N'' up to 14 were observed and in Ref. 20, $N''=18$ has seen; our experiments show some population reaching at least $N''=20$ (although we did not check whether this was produced by single photon photolysis). We excited these OH to specific N' in the $v'=0$ level of the $A\,^2\Sigma^+$ state and observed the fluorescence decay as a function of collider gas pressure. Because it has a relatively small σ_Q, N_2 induces rotational energy transfer (RET) at a rate similar to quenching. To determine the degree of RET that occurred during the decay, high resolution dispersed fluorescence spectra were taken and modeled. Further details on the experimental procedure can be found in Ref. 21.

A nitric acid flow was generated by bubbling He through a 1:2 mixture of a 70% HNO_3 solution in water with a 98% aqueous H_2SO_4 solution. The sulfuric acid served to reduce the vapor pressure of residual water, avoiding contamination of the cell with H_2O. A 150 mTorr background pressure of this gas mixture was maintained throughout the quenching rate experiments, corresponding to ~5 mTorr of HNO_3 vapor. The flow cell was a six-sided stainless steel cross, with collider and nitric acid/helium carrier mixed before entry. Flows were maintained with mass flow controllers such that a fresh mixture entered the laser probe volume for each shot.

The unfocused beam of an ArF laser photolyzed the HNO_3; typical beam energies were 10 mJ per pulse across a 1 cm diameter. A counterpropagating, excimer laser pumped, frequency doubled tunable dye laser used to excite the OH was delayed ~8 μs to allow the molecule to undergo translational relaxation (but only partial rotational relaxation), and to reduce light emission from some two-photon produced photolysis directly into the $A\,^2\Sigma^+$ state. Although optical saturation has no influence on the quenching measurements, the typical ultraviolet pulse energy was 10 μJ in a 5-mm-diam beam to avoid photomultiplier detector saturation.

Fluorescence was collected at right angles, filtered by Schott UG-5 or UG-11 filters to avoid emission from excited NO and NO_2, and detected with a Hamamatsu 1P29 photomultiplier. The filters have uniform bandpass in the 300–320 nm region where the OH emits. A digital oscilloscope processed the time decay signals. For the dispersed fluorescence scans, a Heath f/3.5 monochromator with 50 μ slits was operated in second order, and a boxcar integrator used for averaging.

LIF temporal decays were averaged over 500–1000 shots, and fit to a single exponential between 90% and 10% of signal maximum. Replicate measurements usually varied less than 4%. These were made for 5 to 10 number densities for each collider. All were highly linear with pressure, except for N_2 which showed upward curvature for higher N' at high pressures. This is indicative of some RET occurring, and such cases were fitted to the data at lower collider pressures. The intercepts at zero collider pressure corresponded well in most cases, within ~4%, to well-established radiative lifetimes[22] as a function of N'. However those measured for the highest N' were longer than expected. The lower signal to noise ratios for these experiments increased the importance, in the later portions of the fluorescence decay, from residual fluorescence from an electronically excited NO_2 product of the HNO_3 photolysis.

A more direct determination of the amount of RET occurring in N_2 was made using dispersed fluorescence scans after initially exciting $N'=1$, 3, 7, and 10 for several pressures. Model spectra were made using LIFBASE,[23] which permits nonthermal rotational distributions to be chosen until a best match with experiment is found. More details and figures comparing experimental versus modeled spectra are contained in Ref. 21. For $N'=1$, only about 30% of the population remained in the initially excited level but over 70% did for $N'=10$ at a N_2 pressure of 0.2 Torr, because RET is

TABLE I. OH $A\ ^2\Sigma^+$ quenching rate coefficients, $10^{-11}\ \mathrm{cm}^{-3}\,\mathrm{s}^{-1}$.

Gas	H$_2$	N$_2$	O$_2$	Kr	Xe
N'					
0	...	...	13.3±0.6	...	...
1	20.2±0.9	...	13.2±0.6	...	...
2	18.0±0.9	2.5±0.2	12.9±0.6	6.2±0.4	...
3	...	...	...	...	...
4	15.5±0.9	2.2±0.2	...	3.3±0.3	...
5	...	...	...	...	...
6	...	1.3±0.4	9.7±0.7	2.1±0.1	16.2±0.8
7	11.8±0.7	0.5±0.2	8.9±0.6	...	...
8	...	...	...	1.3±0.3	...
10	6.7±0.6	0.2±0.2	...	0.3±0.2	14.1±1.0
11	...	...	5.6±0.4	...	...
13	...	...	...	0.2±0.1	10.6±0.7
15	5.6±0.4	...	4.5±0.3	...	7.8±0.5
20	4.8±0.4	...	5.0±0.2	0.5±0.2	7.8±0.5

TABLE II. OH $A\ ^2\Sigma^+$ quenching cross sections, Å^2.

Gas	H$_2$	N$_2$	O$_2$	Kr	Xe
N'					
0	...	...	17.7±0.8	...	...
1	10.8±0.5	...	17.5±0.8	...	...
2	9.6±0.5	3.2±0.2	17.2±0.8	9.3±0.6	...
3	...	...	...	...	...
4	8.3±0.5	2.9±0.2	...	5.0±0.4	...
5	...	...	...	...	...
6	...	1.7±0.5	12.9±0.9	3.1±0.2	25.1±1.3
7	6.3±0.4	0.6±0.3	11.9±0.8	...	...
8	...	...	...	1.9±0.5	...
10	3.6±0.3	0.3±0.2	...	0.4±0.3	21.9±1.5
11	...	...	7.5±0.5	...	...
13	...	...	...	0.3±0.2	16.4±1.1
15	3.0±0.2	...	6.0±0.4	...	12.1±0.8
20	2.6±0.2	...	6.7±0.3	0.8±0.3	12.1±0.8

slower for higher N'. Thus, especially for this collider, our σ_Q are not for a pure N'; however, because the rotational level dependence is smooth, and both upward and downward transfer occur, it should be very much representative of the N' initially excited for $N'>3$.

The collision rate coefficients were converted to cross sections by dividing by the average thermal velocity. This of course assumes the OH is translationally thermal. This was checked by increasing the HNO$_3$/He carrier mixture pressure by a factor of 4 for the same collider gas measurements. This leaves a higher amount of total excess energy (32 000 cm^{-1} per photolyzed molecule) in the gas mixture, because the HNO$_3$/He mixture is only a fraction of the total flow. No difference in σ_Q for several colliders and various N' could be observed for the two differing HNO$_3$ concentrations. Were the OH not translationally thermalized, the cross sections would be smaller at the higher HNO$_3$ loading, as they are known to decrease with increasing collision energy.[4,24]

Nitric acid itself is an efficient quencher of the $A\ ^2\Sigma^+$ state. We measured a cross section of 81 ± 8 Å^2 for this collider, exciting into the $N'=1$ level. All subsequent measurements were performed in the dilute HNO$_3$/H3 mixture. The good agreement of the measured decay constants in the absence of added collider with the radiative lifetimes indicated no influence of the carrier mixture on the collider σ_Q.

The other rate coefficients and cross sections are listed, respectively, in Tables I and II, and the σ_Q are illustrated, together with results from other work from our laboratory, in Figs. 1–5. The quoted error bars are those from the fits of quenching rate to collider pressure, and are given at the $1\ \sigma$ level. These provide a reasonable measure of precision when comparing N'-dependent cross sections for a given collider. There is somewhat more error when comparing cross sections among colliders. We have not undertaken an absolute error analysis, but expect absolute cross sections to be accurate to within the quoted error bars plus about 10% for low N' and 20% for higher N', where signal levels are lower. These absolute errors are based on a thorough error analysis in the study of temperature-dependent VET and quenching,[9,25] a very similar experiment performed on the same apparatus.

DISCUSSION

Our results may be compared with other studies from this laboratory for low N'. For O$_2$, N$_2$, and H$_2$, the results of Copeland et al.[2] are included in Figs. 1–3. For O$_2$, the disagreement at lowest N' is probably due to RET in our experiment, Copeland et al.'s results are to be preferred because lower pressure was used in those experiments. For H$_2$, the results agree well. For N$_2$, an important collider, the two sets of results agree to within error bars although the present results appear to generate a smoother overall pattern for $N'=4$ and 6, for which the signal levels were low in Ref.2. A thermal value at 344 K by Heard and Henderson[26] is 3.4 ± 0.3Å^2. Because such a distribution has some population at higher N', it would be expected to have a smaller σ_Q than one for pure or nearly pure $N'=2$, and is thus in agreement.
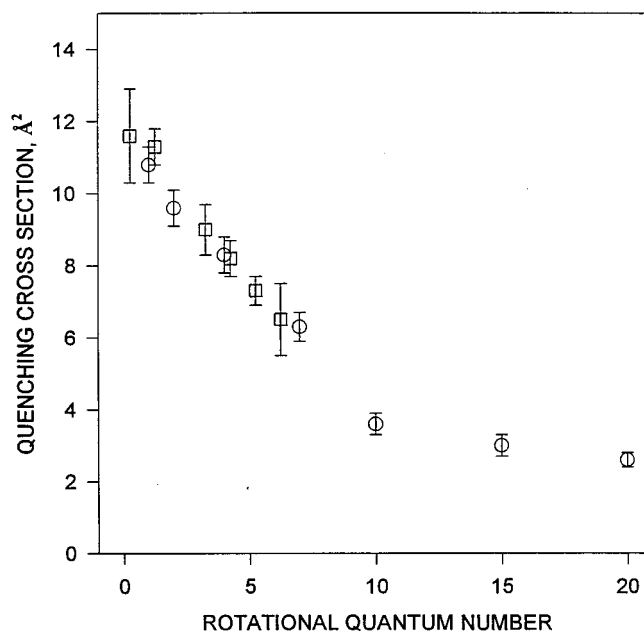
HYDROGEN QUENCHING

FIG. 1. Quenching by hydrogen. Circles, this experiment, with error bars from fitting curves only. Squares, Copeland et al., Ref. 2.

3102   J. Chem. Phys., Vol. 115, No. 7, 15 August 2001

Hemming *et al.*
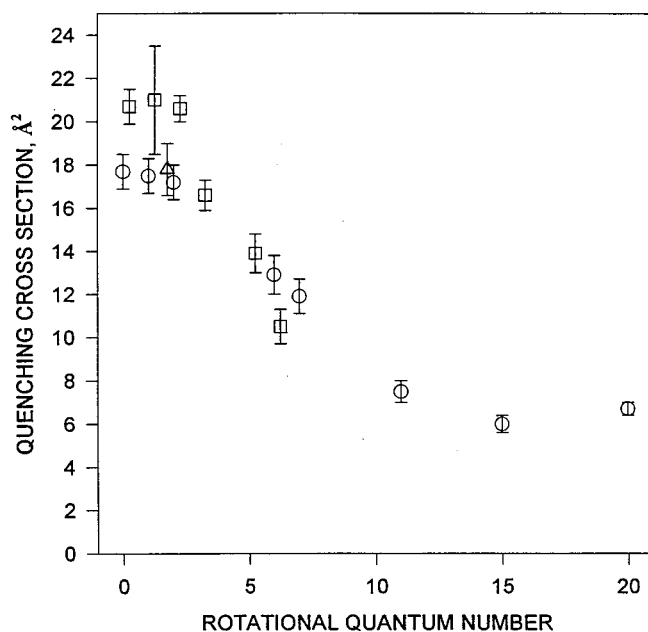
OXYGEN QUENCHING

FIG. 2. Quenching by oxygen. Circles, this experiment. Squares, Copeland *et al.*, Ref. 2. Triangle, quenching for a 300 K distribution, Wysong *et al.*, Ref. 18.
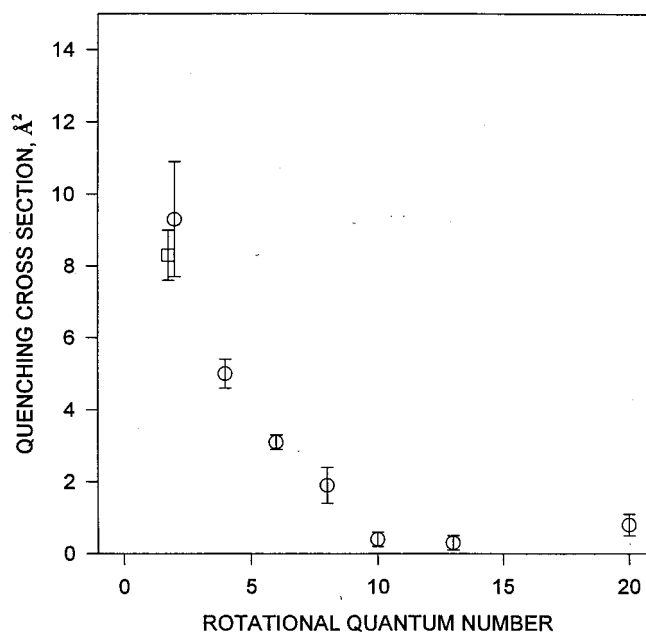
KRYPTON QUENCHING

FIG. 4. Quenching by krypton. Circles, this experiment. Square, quenching for a 300 K distribution, Wysong *et al.*, Ref. 18.

For the rare gases, no single level studies have been made previously; thus we compare those for particular rotational distributions. Wysong *et al.*[18] made measurements in a thermally relaxed distribution, peaking at $N'=2$ for 300 K. Our and her results are shown for Kr in Fig. 4 and Xe in Fig.

5. For Kr, our results at $N'=2$ is in good agreement with that of Wysong *et al.* 8.7 ± 0.7 A^2. Heard and Henderson[26] measured a thermal value of 8.5 ± 0.6 Å^2 for this collider, also in good agreement. Rohrer and Stuhl[27] have measured σ_Q for Kr and Xe colliders, with the A $^2\Sigma^+$ state of OH formed
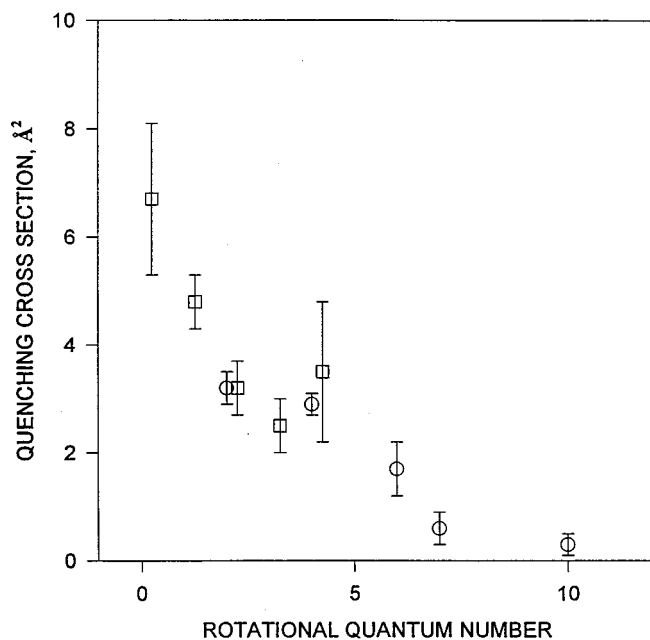
NITROGEN QUENCHING

FIG. 3. Quenching by nitrogen. Circles, this experiment. Squares, Copeland *et al.*, Ref. 2.
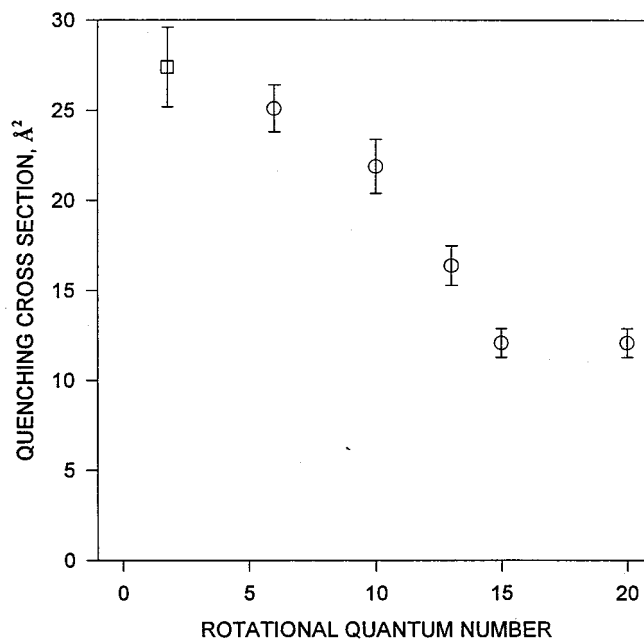
XENON QUENCHING

FIG. 5. Quenching by xenon. Circles, this experiment. Square, quenching for a 300 K distribution, Wysong *et al.*, Ref. 18.

directly by multiphoton dissociation of HNO_3. This process produces a near thermal distribution characterized by a temperature of 3760 K, corresponding to a distribution peaking near $N'=8$. They found cross sections for Kr and Xe of 2.4 and 15.6 Å^2, which may be compared with values of 2 and 23 Å^2 found here for that rotational level.

The plots show that σ_Q for H_2, O_2, and Xe drop with N' but reach a constant plateau at high N'. N_2 and Kr appear to behave differently. For these colliders, the cross sections also decrease with N' but appear to drop to zero or nearly zero within error bars at $N'=10$. (The value of 0.8 ± 0.3 measured $N'=20$ for Kr collider includes fitting errors only, and this experiment was performed at very low signal level. Thus this may not be statistically different from zero.) Thus, for all the colliders, the results are in agreement with expectations based on a washing out of highly attractive collision complex formation entrance channels on an anisotropic surface. This was true of NH as well.[6] At high N', however, one would expect some nonzero cross sections because the average surface should remain generally attractive. Therefore we find the decrease to zero or near zero cross sections above $N'=10$ for N_2 and K r to be puzzling. Perhaps for this pair, which have the lowest σ_Q of all five colliders studied, the average surface is not attractive enough for efficient complex formation at high N'. However, the $A\ ^2\Sigma^+$ OH–Ar van der Waals complex[15] has an attractive maximum depth of some 1000 cm^{-1}. It is difficult to think that the $A\ ^2\Sigma^+$ OH–Kr surface would be less attractive. The $A\ ^2\Sigma^+$ OH–N_2 van der Waals complex also shows an attractive surface.[17]

Ab initio calculations have been made for the interactions of OH (X) and OH (A) with N_2 and H_2 and are presented in Ref. 17. These show that particular orientations of the surface for the OH and the collision partner have attractive wells, and that one of the orientations in each case produces an OH$(A\ ^2\Sigma^+)$–M surface that has a conical intersection with an OH$(X\ ^2\Pi_i)$–M surface. In the case of N_2 as the collider, the orientations are linear O–H–N–N and H–O–N–N. The former well in the A state, albeit deeper, has a barrier before it crosses the potential for the ground state, so it does not quench. However, the H–O–N–N upper state potential crosses the ground state potential some 2000 cm^{-1} below the asymptotic energy, leading to quenching.

The case of H_2 is especially interesting from this point of view. Here the wells in the ground and upper states are both T-shaped with the H of O–H pointing to the center of the H_2 bond. These, however, do not intersect below the asymptotic energy of the upper state. If the OH is rotated 180° into the opposite T-shaped configuration, H–O–H_2, then a conical intersection exists leading both to OH(X) + H_2 and the H_3O surface, which rapidly forms the chemical reaction product H_2O. In spectroscopic van der Waals experiments, the upper state complex is formed in the O–H–H_2 form because it is directly excited from that configuration in the OH(X)–H_2 complex. Thus, to quench (or react) the OH in the upper state must go internal rotation around a small barrier to be oriented as H–O–H_2. From here it can cross into both surfaces. In a recent experiment, Anderson *et al.*[28] have shown that chemical reaction is an important part of the loss process in

OH$(A\ ^2\Sigma^+)$ + H_2, through observation of the H atom product through two-photon LIF.

The spectroscopically prepared complexes are in one orientation and may need to shift to the other to undergo quenching/reaction in those half collision events. This is consistent with the typical 4 ps lifetimes observed for OH(A)–H_2 complexes through line broadening.[17] In our full collision flow cell experiments, the colliders necessarily average over all impact parameters and approach angles. Here the rotational dependence we observe of the quenching (and, in the case of H_2, reaction) would then depend on the entrance channel of the collision. A slowly rotating OH presents a smaller barrier to the H_2 ''finding'' that orientation which is suitable for quenching. As the OH rotates more quickly, the surface appears more isotropic to the collider and the facilitation of a favorable orientation is lessened.

SUMMARY

Quenching of the $v'=0$ level of the $A\ ^2\Sigma^+$ state of the OH radical has been studied as a function of rotational level at high N' and a temperature of 300 K. The cross sections decrease as N' increases, in general accord with expectations based on an anisotropic attractive potential surface.

ACKNOWLEDGMENTS

[1] I. S. McDermid and J. B. Laudenslager, J. Chem. Phys. **76**, 1824 (1982).
[2] R. A. Copeland and D. R. Crosley, Chem. Phys. Lett. **107**, 295 (1984); R. A. Copeland, M. J. Dyer, and D. R. Crosley, J. Chem. Phys. **82**, 4022 (1985).
[3] R. K. Lengel and D. R. Crosley, Chem. Phys. Lett. **32**, 261 (1975); J. Chem. Phys. **68**, 5390 (1978).
[4] D. R. Crosley, J. Phys. Chem. **93**, 6273 (1989).
[5] N. L. Garland and D. R. Crosley, J. Chem. Phys. **90**, 3566 (1989).
[6] E. L. Chappell, J. B. Jeffries, and D. R. Crosley, J. Chem. Phys. **97**, 2400 (1992).
[7] P. O. Wennberg, R. C. Cohen, N. L. Hazen, L. B. Lapson, N. T. Allen, T. F. Hanisco, J. F. Oliver, N. W. Lanham, J. N. Demusz, and J. G. Anderson, Rev. Sci. Instrum. **65**, 1848 (1994).
[8] R. A. Copeland and D. R. Crosley, J. Chem. Phys. **84**, 3099 (1986).
[9] K. L. Steffens and D. R. Crosley, J. Chem. Phys. (submitted).
[10] L. R. Williams and D. R. Crosley, J. Chem. Phys. **104**, 6507 (1996).
[11] B. L. Hemming and D. R. Crosley, J. Phys. Chem. (to be published).
[12] E. L. Hintsa, E. M. Weinstock, J. G. Anderson, R. G. May, and D. F. Hurst, J. Geophys. Res. **104**, 8183 (1999).
[13] K. J. Rensberger, J. B. Jeffries, R. A. Copeland, K. Kohse-Höinghaus, M. L. Wise, and D. R. Crosley, Appl. Opt. **28**, 3556 (1989).
[14] M. D. Rumminger, R. W. Dibble, N. H. Heberle, and D. R. Crosley, *Twenty-Sixth International Symposium on Combustion* (The Combustion Institute, Pittsburgh, 1966), p. 1755.
[15] A. Degli-Esposti and H.-J. Werner, J. Chem. Phys. **93**, 3351 (1990).
[16] A. Jörg, A. Degli-Esposti, and H.-J. Werner, J. Chem. Phys. **93**, 8757 (1990).
[17] M. I. Lester, R. A. Loomis, R. L. Schwartz, and S. P. Walch, J. Phys. Chem. **101**, 9195 (1997).

[18] I. J. Wysong, J. B. Jeffries, and D. R. Crosley, J. Chem. Phys. **92**, 5218 (1990).

[19] G.-H. Leu, C.-W. Hwang, and I.-C. Chen, Chem. Phys. Lett. **257**, 481 (1996).

[20] A. Jacobs, K. Kleinermanns, H. Kuge, and J. Wolfrum, J. Chem. Phys. **79**, 3162 (1983).

[21] B. L. Hemming, Ph.D. thesis, Stanford University, June 1998.

[22] J. Luque and D. R. Crosley, J. Chem. Phys. **109**, 439 (1998).

[23] J. Luque and D. R. Crosley, LIFBASE: Database and Spectral Simulation Program, SRI International Repot No. MP 96-001, 1996.

[24] P. W. Fairchild, G. P. Smith, and D. R. Crosley, J. Chem. Phys. **79**, 1795 (1983).

[25] K. L. Steffens, Ph.D. thesis, Stanford University, December 1994.

[26] D. E. Heard and D. A. Henderson, Phys. Chem. Chem. Phys. **2**, 67 (2000).

[27] F. Rohrer and F. Stuhl, Ninth International Symposium on Gas Kinetics, Bordeaux, France, July 1986.

[28] D. T. Anderson, M. W. Todd, and M. I. Lester, J. Chem. Phys. **110**, 11117 (1999).