ROTATIONAL AND TRANSLATIONAL EFFECTS IN COLLISIONS OF ELECTRONICALLY EXCITED DIATOMIC HYDRIDES

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ABSTRACT

Collisional quenching and vibrational energy transfer proceed competitively with rotational energy transfer for several excited states of the diatomic radicals OH, NH, and CH. This occurs for a wide variety of molecular collision partners. This phenomenon permits the examination of the influence of rotational motion on the collision dynamics of these theoretically tractable species. Measurements can also be made as a function of temperature, i.e., collision velocity. In OH ($A^2\Sigma^+$), both vibrational transfer and quenching are found to decrease with an increase in rotational level, while quenching decreases with increasing temperature. This behavior indicates that for OH anisotropic attractive forces govern the entrance channel dynamics for these collisions. The quenching of NH ($A^3\Pi_i$) by many (although not all) collision partners also decreases with increasing rotational and translational energy, and NH ($c^1\Pi$) behaves much like OH ($A^2\Sigma^+$). However, the quenching of CH ($A^2\Delta$) appears to decrease with increasing rotation but increases with increasing temperature, suggesting in this case anisotropic forces involving a barrier or repulsive wall. Such similarities and differences should furnish useful comparisons with both simple and detailed theoretical pictures of the appropriate collision dynamics.

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Introduction

For reasons of both fundamental and practical interest, collisions of the electronically excited states of diatomic hydrides, particularly the hydroxyl radical, have been the subject of many studies by diverse means over many years. With modern laser methods, individual vibrational and rotational quantum levels, or reasonably well-defined distributions over such levels, can be initially selected within these excited states. In many cases the rates of quenching, vibrational and rotational energy transfer, and translational thermalization are all competitive, that is, they occur on similar time scales. This enables the study of the influence of one of these forms of energy on collisions involving relaxation of a different mode, e.g., the rotational level dependence of vibrational energy transfer. This situation stands in sharp contrast to that observed for ground electronic states, where rotational and translational thermalization typically take place some hundred times faster than vibrational transfer, thereby preventing such an examination.

The first of such studies was that of downward vibrational energy transfer (VET) in the $A^2\Sigma^+$ state of the OH and OD radicals.[1,2] For the simple colliders H_2, D_2, and N_2, the VET cross sections were found to be on the order of gas kinetic, and to decrease sharply with increasing rotational level. This rapid rate of transfer, together with other evidence discussed below, suggested that attractive forces and the formation of a transitory collision complex played a role in the VET process, while the dependence on rotational level indicated that those forces were anisotropic in nature. Because the A-state of OH has a large dipole moment, 2D, an anisotropic attractive interaction between it and a collision partner is not surprising. Subsequently, it was found that for the colliders N_2 and O_2, quenching of OH $A^2\Sigma^+$ varies with rotational level in a similar way,[3] and that for many quenchers the cross sections decrease with increasing temperature (i.e., collision velocity).[4] Thus anisotropic attractive forces appear important in this process as well.

Investigations of quenching of the $A^3\Pi_i$ and $c^1\Pi$ states of NH, and the $A^2\Delta$ and $B^2\Sigma^-$ states of CH, show a dependence on rotational level, while quenching of both those states of NH, the $A^2\Delta$ state of CH, and the $A^3\Pi_i$ state of PH vary with temperature. However, for these radicals the interpretation is not as simple and, for CH at least, quenching appears to involve repulsive forces or a barrier.

This paper reviews the experiments investigating these effects of rotational and translational energy on VET and quenching in the diatomic hydrides, and speculate on possible reasons for such behavior. Many of the ideas developed from experiments conducted on the OH radical, and the concepts thus involve the attractive forces noted above. One of the reasons for studying the other hydrides was an attempt to generalize from the findings on OH, but matters turned out to be more complicated and thus more interesting. Recognize also that these hydrides present us fortunate opportunities in another respect, that is, for at least small collision partners, they are amenable to detailed calculation of potential surfaces and trajectories. Such computations can be expected to be realistic even for excited states of the radicals. Thus we can not only develop elementary concepts concerning these collisions, but also use the results to test predictions from sophisticated theories, particularly when we compare different electronic states of different hydrides.

This is not intended as a review of the field of diatomic hydride collisions as a whole, but is specialized to the rotational and translational effects on quenching and VET, and the information these effects convey concerning molecular interactions. Earlier work on OH and NH has been summarized in the reviews of Schofield[5] and Slanger,[6] respectively. Occasionally, large discrepancies among measurements reported from different laboratories can be seen; in at least some cases this can be attributed to unrecognized effects arising from the rotational and/or translational dependence. These interesting state-specific effects have immediate practical implications in determining fluorescence quantum yields for the large number of studies in which these radicals are detected in practical systems, using the method of laser-induced fluorescence (LIF). These include measurement of OH, NH and CH for combustion applications[7] and monitoring of the OH radical in the troposphere[8] or stratosphere.[9]

Two conventions will be utilized throughout. First, the term quenching is used to denote total removal of the molecule from a given electronically excited state. This process, whose collisional rate is measured by the loss of fluorescent photons either on a time-dependent or steady-state basis, can include chemical reaction as well as conversion to the nonradiating ground state and/or other excited states. VET is considered a distinct and different process, occurring wholly within a particular electronic state. Second, from the pressure (density) dependence of a pseudo-first order decay rate, one obtains a rate constant k in units of $cm^3\ s^{-1}$. This term contains an uninteresting dependence on mass and temperature through the collision velocity, $<v> = \sqrt{8kT/\pi\mu}$. We can better examine the effects of different colliders and the influence of collision energy on the effective interaction between the radical and collider through the "thermally averaged" cross section $\sigma = k/<v>$, in units of cm^2, or as usually used here, $Å^2$. A subscript R, V or Q on k or σ indicates the type of process: rotational energy transfer (RET), VET, or quenching.

Rotational Level Dependence and Collision Complex Formation in OH VET

The rotational dependence of collisions of a diatomic hydride was first apparent in experiments on VET in the $A^2\Sigma^+$ state of the hydroxyl radical.[1,2] These measurements were made using spectrally resolved fluorescence scans of laser-excited OH. The discharge flow system utilized is typical of those employed for many of these studies. Hydrogen atoms are produced by a microwave discharge in H_2 or H_2O; these are then reacted with NO_2 to form the OH molecules. Collision partners are added downstream of the radical production region and their densities monitored by pressure gauges and flowmeters. Enough time is allowed to permit the ground state radicals and the colliders to mix and to reach translational and rotational thermalization with the cell walls, the latter condition checked by LIF excitation scans which measure the rotational population distribution within the ground state.

In these VET experiments, the beam from a pulsed tunable laser was directed into the cell, exciting the OH to the v' = 1 vibrational level of the A-state. This ultraviolet transition, near 282 nm, requires the use of frequency-doubled dye laser radiation. Typical laser pulse durations in current LIF experiments of this type are 10 ns. The laser was tuned to a line sufficiently isolated spectrally that a single rotational level in the upper state was populated by the laser. The fluorescence at right angles was collected with a lens system, dispersed with a scanning monochromator, and detected with a photomultiplier. It was then processed with a gated integration system which recorded signal only during and shortly after the laser pulse, thereby avoiding background noise (dark current and light from the discharge) during the long period between laser pulses, which occur at typical repetition rates of tens of Hz.

A fluorescence spectrum from this experiment is shown in Fig. 1. Here, the electronic gate is set long enough to integrate in time over the entire time evolution of the fluorescence pulse which, in the presence of no added collider, occurs with a decay time of about 700 ns. This spectrum was obtained in about 1 Torr added H_2 collider. The lines to the right of 3124 Å are primarily the (1,1) band, emitted by radicals in the initially pumped v' = 1 level, while the denser spectrum at shorter wavelengths is the (0,0) band, due to OH molecules in the v' = 0 level populated by VET collisions with the hydrogen. Note that the (1,1) band comprises five strong lines and a few much smaller ones. The strong lines all arise from the initially pumped rotational level N' = 3, and their predominance shows that little RET has occurred within v' = 1. However, the intensity of the (0,0) transition indicates that considerable VET has taken place. Because most of the OH molecules which remain in v' = 1 at this pressure are still in N' = 3, most of those which have undergone VET have come from N' = 3 as well, and the measured VET cross section, σ_V, will be specific to that particular level. This competition in which RET is slower than VET, illustrated clearly in Fig. 1 for collisions with H_2, is the basis for the ability to determine rotational-state-specific cross sections for VET and quenching in the diatomic hydride radicals. The intensities of the fluorescence in the two bands seen in Fig. 1 can be integrated to furnish the populations in the two vibrational levels, which are then readily analyzed to yield the VET cross sections.

For the colliders H_2, D_2, and N_2 the σ_V are large, 10 to 25 Å^2 for the lowest rotational level, N' = 0. Further, the σ_V were found to decrease sharply with increasing N', falling in the case of N_2 a factor of two between N' = 0 and 5. The results for H_2 and N_2 are given in Fig. 2, plotted in the form $\ln[\sigma_V]$ vs. $N'(N' + 1)$, a wholly empirical relationship discussed later. This phenomenon was attributed to the formation of a transitory collision complex with entrance channel dynamics dominated by anisotropic attractive forces.[1,2] The lifetime of this complex is not specified but is longer than a rotational period, and lengthy enough to permit a significant amount of scrambling of energy among the different vibrational, rotational, and translational degrees of freedom of both the OH and the collision partner.

The evidence for such a complex is as follows.[2] The first is simply the large size of the σ_V, with a range appropriate to interactions of a highly polar species like A-state OH. This is not caused by resonant energy exchange. This can be seen by comparing the VET cross section of 15 Å^2 by D_2, whose vibrational spacing matches that of OH within 4 cm^{-1}, with the σ_V of 10 Å^2 for H_2 which has an energy mismatch of 1460 cm^{-1}. Similar arguments can be applied to N_2 relaxing OH and OD; further, the σ_V vary smoothly with N' (see Fig. 2), not irregularly as might be expected for resonances dependent upon detailed vibrational-rotational level spacings. Altogether, the cross sections are not strongly dependent upon isotope, indicating that the internal level structure of the collision partner plays little role. (On the other hand, the complexes are not so long-lived as to facilitate chemical exchange, e.g., between D_2 and OH to yield excited OD.) The rotational population distribution in $v' = 0$, of OH molecules which have undergone VET, can be described by a temperature, albeit one which is hotter than the gas temperature: 600 to 700 K for H_2 and D_2, and 900 K for N_2. Further, this distribution appears independent of the N' initially excited in $v' = 1$. This suggests a partial conversion of OH vibrational energy into OH rotational energy, but in a statistical way as might be expected with rapid energy flow in the four-atom complex. Measurements were also made of the rate of transfer from $v' = 2$. Although less accurate because of poorer knowledge of the rotational distribution in $v = 1$ resulting from $2 \rightarrow 1$ transfer, they showed definitively for N_2 that $\sigma_V(2\rightarrow1) \sim \sigma_V(2\rightarrow0) \sim \sigma_V(1\rightarrow0)$. Relaxing 5800 cm^{-1} of vibrational energy as easily as 3000 cm^{-1} cannot be readily explained in conventional pictures of VET involving a purely repulsive interaction potential. Thus there are several separate facts, all indicating the existence of a collision complex in VET of $A^2\Sigma^+$ OH molecules, a picture which underlies many of the subsequent concepts and postulates (though not always the results) concerning collisions of excited diatomic hydrides.

Within this framework of collision complex formation, the rotational level dependence was explained as follows.[1,2] The polar nature of the OH molecule leads to a highly anisotropic surface, having in some orientations deep attractive valleys which can lead to more efficient complex formation and thereby enhance the VET process. When the OH is not rotating, it and the collider can easily find these valleys and lock together to form the complex. As the OH rotates, however, it averages over the surface during the approach of the collision pair, and washes out the influence of these particularly efficacious regions. Thus the decrease in σ_V with increasing N' is due to a decrease in the cross section for complex formation. Trajectory studies[10] on vibrational transfer in HF-HF collisions indicated that such a mechanism could be operative, although no such state-specific experimental evidence is available on that system. The OH results are also in accord with the finding that σ_Q is independent of the fine structure level associated with each rotational level in this $^2\Sigma$ state, that is, the effects are due to the mechanical rotation of the radical.

VET in A-state OH was further studied by German,[11] who at the same time investigated quenching by measuring the time dependence of the fluorescence signals. For this purpose, a signal integrator gate width of 50 ns was used and the time delay between the laser pulse and the gate varied to trace out the decay curve. With increasing collider density and collisional removal of the excited state, the decay constant becomes progressively faster; its slope when plotted vs. density furnishes the rate constant for the removal process. Fig. 3 shows such plots (taken from a later quenching study described below). The vibrationless $v' = 0$ level can decay only by quenching and radiation. $v' = 1$ can be collisionally removed by both quenching and VET; a combination of lifetime and fluorescence intensity measurements is necessary to determine both cross sections. German found that the total removal ($\sigma_V + \sigma_Q$) from $v' = 1$ decreased with increasing N' for the three colliders H_2, N_2, and O_2, in general agreement with the results of Ref. 1.. A decrease of σ_Q for both $v' = 1$ and 0 with increasing N' was also indicated, although the reported variation is often less than the accompanying uncertainties.

In only two other studies, both of which are much more recent, has collider-specific VET of $A^2\Sigma^+$ OH (or any other radical) been studied in sufficient detail to permit an examination of the rotational level dependence. These studies again used combinations of fluorescence scans and time decay measurements. N_2, O_2, and H_2O, the important colliders for atmospheric monitoring purposes, were investigated by Burris et al.[12] while collisions with H_2O, NH_3, CO_2, CH_4, N_2O, N_2, SF_6, and CF_4 are described in Ref. 13. In general, the findings are in good agreement among all four of these collider-specific flow cell investigations. The total decay from the excited state decreases with increasing N' for all colliders (save the highly polar H_2O and NH_3, for reasons discussed below). A rotational distribution in v'=0 described by a temperature of 750 K for N_2 collisions was found in Ref. 13, similar to that reported in Ref. 2. However, a close examination of the spectra for different initially excited N' in v' = 1 does reveal small differences (see also Ref. 14, for spectra under lower resolution), suggesting a weak memory.

The variation in σ_V and $\sigma_{Q,v=1}$ were separately determined for CO_2 (Ref. 13) and for N_2 and O_2 (Ref. 12). For all three colliders it appears that σ_V decreases less rapidly with N' than does $\sigma_{Q,v=1}$, although in each case 2-σ error bars are compatible with equal variation. If a collision complex is formed which then leads to both VET and quenching, the variation of the cross section with N' should be the same for each process. If different, the dependence for both processes cannot be governed solely by an anisotropic, attractive interaction. This point, although not outside the uncertainties in a difficult experiment, is a worrisome inconsistency in an otherwise understandable body of data on VET in $A^2\Sigma^+$ OH. It deserves further, more careful investigation for these colliders and others.

The rotational dependence of VET of OH has also been studied in a flame at atmospheric pressure,[15] using steady-state fluorescence intensity ratios. CH_4 was burned in air, and the OH was excited near the flame front region, so that a variety of collision partners were present and some temperature gradient was likely sampled. Spectrally resolved fluorescence furnished relative σ_V, which were found to decrease with N' similarly to the flow cell results.

Attractive Forces and Rotational Level Dependence in OH Quenching

McDermid and Laudenslager,[3] also motivated largely by quantum yield considerations for atmospheric monitoring of OH, used the time dependence of the decay of total, unfiltered fluorescence from the v' = 0 level to determine quenching cross sections σ_Q for the colliders N_2, O_2, H_2O, and H_2. A two-chamber flow cell with differential pumping maintained the background gas pressures from the OH production at very low values. A transient recorder was used to record the decay traces at different collider pressures. This work was the first in which a rotational level dependence of the quenching could be unambiguously discerned. It was observed for N_2 and, less markedly, for O_2. In addition, the measured cross sections are similar in size to the σ_V reported in Refs. 1, 2, and 11. This suggested that quenching too is governed by anisotropic, attractive forces.

A more extensive study of these effects was conducted in our laboratory. The cell was also differentially pumped, similar in design to that of McDermid and Laudenslager. A scanning gated integrator was used in the first set of measurements,[16] in which a larger set of rotational levels was studied for the same collision partners and for the deuterated species D_2 and D_2O. A later series of measurements[17] utilized a transient digitizer, and included OD and a much larger set of colliders. The findings were largely in accord with expectations from the VET results: large cross sections for most colliders, varying in a manner consistent with attractive forces (this could also be anticipated from measurements of σ_Q at elevated temperature[4] as discussed below); identical behavior for deuterated and protonated species; and a nearly universal decrease of σ_Q with increasing N'.

We first consider the role which attractive forces play in the quenching process. Unlike VET, where we could examine cross sections for different v', a lack of resonance effects, etc., we have here only the variation in cross section among collider (and the temperature dependence discussed below). The lack of isotope dependence indicated that the quenching is governed not by internal levels but by electronic interactions, and prompted a simple theoretical examination in terms of attractive forces, and collision complex formation.[4,17] One such picture, suggested by Parmenter and coworkers,[18] correlates the cross section with the well depth of the radical-collider interaction. The only experimental well depth for these excited radical colliders is from a recent study of $OH(A^2\Sigma^+)$-Ar van der Waals complexes.[19] A strongly attractive 700 cm^{-1} deep well and several bound vibrational levels were found. For the molecules studied here, the radical-collider well depths had to be estimated for correlation purposes by the square root of the collider-collider well depth, usually obtained from boiling point data. For OH some correlation can be found.[4]

However, more successful was an approach adapted from that used by Lee and coworkers[20] to describe quenching in SO_2. The model was formulated in terms of attractive interactions involving multipole moments between the excited OH and the collider. These r^{-2}, r^{-4}, and r^{-6} interactions arise from dipole-dipole, dipole-quadrupole, and dipole-induced dipole plus dispersion forces respectively; they can be calculated from known (or reasonably estimated, if necessary) dipole and quadrupole moments, polarizabilities and ionization potentials. In addition, the potential includes a repulsive centrifugal barrier $l(l + l)/r^2$, where the collisional angular momentum l can be expressed in terms of the collision energy and impact parameter. If, for a given energy, the impact parameter is small enough, the collision pair can surmount this barrier and form a complex; as it later dissociates, it will form $X^2\Pi_i$ OH part of the time (probability P) and form $A^2\Sigma^+$ OH the rest of the time. For this simple one-dimensional potential, trajectories can be readily calculated and integrated over a thermal velocity distribution (see Ref. 4) to yield a thermally averaged cross section σ_{CF} for complex formation. Then $\sigma_Q = P\sigma_{CF}$. There is no reason a priori to expect P to be the same for each collision partner, although a large variation among colliders would invalidate the idea of a collision governed predominantly by attractive force, entrance channel dynamics.

A plot of σ_Q vs. σ_{CF} for $A^2\Sigma^+$ OH shows a good correlation for many colliders, with a value of $P = 0.5$ at room temperature.[17] Notable exceptions are CF_4 and SF_6, for both of which σ_{CF} is near 80 Å^2 but experimental upper limits give $\sigma_Q < 3$ Å^2. Also, N_2 has a conspicuously low P value near 0.1. It was suggested that each of these molecules is efficient at complex formation but inefficient at mixing the Σ and Π states during the lifetime of the complex. One would then expect them to be efficient at VET, which depends only on energy redistribution and not state mixing. N_2 was already known[1,11] to have a large σ_V, and this was later found to be true for the fluorinated species as well.[13] For large molecules, including an isomeric set of butenes, the model does not work.[21] Here, the quenching cross sections are larger than the calculated σ_{CF}, a result attributed to a breakdown in the ability to describe these molecules by simple pointwise multipole moments. In spite of these exceptions, it appears safe to conclude that the quenching of $A^2\Sigma^+$ OH, like VET in the same state, is often controlled by attractive forces, which depend on interactions among the electronic wavefunctions but not strongly on the internal vibration-rotation level structure of the collider pair.

This simple model considered only a one-dimensional potential, with the nonrotating OH and its collision partner aligned in the most favorable orientation. All of the attractive forces except dispersion involve the direction of the dipole moment of the OH so that one expects a high degree of anisotropy. Attractive forces with distinctive anisotropy are evident in an ab initio calculation[22] of the potential for OH ($A^2\Sigma^+$) interacting with CO ($X^1\Sigma^+$). Thus one does indeed expect valleys in the potential surface, along which the approach is especially favorable. Huo[23] assembled a simple model potential with dipole-dipole interactions in two different directions, elaborating on our qualitative picture. These trajectory calculations showed a 25% decrease in σ_Q as N' increased from 0 to 5.

A plot of decay constant vs. pressure of added CO_2, for both OH and OD in v' = 0, taken from Ref. 17, is shown in Fig. 3. The slope, i.e., value of σ_Q, clearly varies strongly with rotational level. Cross sections were measured for nineteen colliders, and a significant rotational level dependence was found for all but the rapid quenchers C_2H_6, C_2H_4, C_2H_2, and CCl_4, for which σ_Q is between 80 and 120 Å^2. The rotational effects were studied for both isotopes with CO_2 (Fig. 3) and N_2O, the colliders exhibiting the largest N' dependence, in the hopes that some mechanistic insight might be gained. The cross sections are plotted in Fig. 4 in the form $\ln[\sigma_Q(N')]$ vs. the variable BN' (N'+ 1), i.e., the rotational energy. Both isotopic forms fit on the same plot; plots vs. BN', that is, the rotational frequency, do not show as good a correlation. Cross sections with other collision partners, plotted as in Fig. 4, also produce straight lines. The results of Ref. 2, for $v' = 1 \rightarrow 0$ VET for collisions with N_2 and H_2 are examined in the same way in Fig. 1. It appears that the mechanism producing the rotational dependence is the same for both quenching of $v' = 0$ and VET from $v' = 1$.

This correlation, however, does not reveal the details of this mechanism for there is yet no theoretical basis for this or any other type of dependence on rotational energy. Conclusions may be drawn by fitting data to some established relationship; however, an unknown relationship cannot be proven in this manner. We stress that, although this correlation with the rotational energy is reminiscent of an energy gap law, that simple picture is not applicable here. In the process of VET or quenching of $A^2\Sigma^+$ OH, some 3000 cm^{-1} of vibrational or 30000 cm^{-1} of electronic energy, respectively, is converted into other forms. The OH internal energy thus changes considerably, much more than the maximum value of 500 cm^{-1} of rotational energy variation involved here. Perhaps the relationship illustrated in Figs. 1 and 4 can be explained in simple theoretical terms, perhaps insight into its meaning requires investigation through complex numerical trajectory computations on realistic surfaces. We believe that it does reflect the behavior of the collision partners sampling the entrance region to the potential surface(s) on which both quenching and VET take place, and hope that such state-specific results will provide detailed, useful comparison with theory.

Rotational Level Dependence of Quenching in NH

The first direct investigation of the rotational level dependence of quenching in a hydride other than OH was performed by Hofzumahaus and Stuhl[24] on the $A^3\Pi_i$ state of the NH radical. Sequential multiphoton photolysis of NH_3 by an ArF laser at 193 nm produced the NH directly in the excited state; the nascent rotational distribution was nonthermal but well-defined with a maximum population between N' = 8 and 13. Quenching was then determined from the pressure dependence of the time decays of the resulting fluorescence emission following the photolysis laser pulse. A monochromator dispersed the fluorescence, with a wide exit slit to detect all Q-branch lines of the (0,0) band. This avoided potentially complicating effects in the observed time (and pressure) dependence due to RET among the A-state levels.

Although the translational energy was not measured directly in this experiment, there is little available from the dissociation process, so the collision temperature is likely near 300 K. (Because σ_Q can depend on both rotation and translation, it is important that both distributions be specified when comparing results. This is often not possible and has caused confusion in the past; see Ref. 25 for a discussion of this point concerning various NH quenching measurements.) Addition of ~100 Torr N_2, found to be a very inefficient quencher of A-state NH, cools the rotational levels to a 300 K distribution. In this way, σ_Q were determined for distributions over both high and low rotational levels for the colliders H_2 and NH_3; σ_Q was higher by 50% for the lower N'. A subsequent study[26] included CO and O_2 quenchers and Ar relaxer, with similar results. The cross sections are about half those measured for $A^2\Sigma^+$ OH with the same colliders, and suggest at least for NH_3 a significant role of attractive forces. Thus the same mechanism probably governs the rotational level dependence in both hydrides. For CO_2 no dependence on rotational level was found.[26,27] However, the cross section for this collider is much smaller, only 1 Å^2 compared with 70 Å^2 for OH in N' = 0, and rotational thermalization likely occurs before quenching thus preventing the observation of any rotational-level-dependent σ_Q.

Quenching of single rotational levels was investigated using LIF excitation of NH produced in a discharge flow system;[25] the experimental method and apparatus were the same used for the OH measurements of Ref. 17. Nine collision partners were investigated; of these, all but CO_2 and N_2O showed a rotational level dependence. With the exception of these last two colliders, the cross sections are between 7 and 100 $Å^2$ and show some though not impressive correlation with either the well-depth or multipole model calculations. σ_Q for H_2O and D_2O are the same (as are those for H_2 and D_2 measured for a thermal distribution at high temperature[28]), indicating again that the internal levels of the collider are unimportant. From these rotational-level-specific results[25] one can calculate an effective σ_Q for a 300 K rotational distribution to compare with the values measured directly for a thermal distribution. The calculated cross sections are between 10 and 20% larger than those of Refs. 24 and 26 for H_2, CO, O_2, C_2H_6, H_2O and NH_3, and the same for CO_2, constituting reasonable agreement between two very different methods of determining the same quantity. Recently,[29] sequential multiphoton photolysis of NH_3 to produce ground state NH has been followed by single-level LIF excitation, to directly measure σ_Q (N') for NH_3 collider. Linewidth measurements[30] indicate a translational temperature below 900 K. The results from the Bochum and SRI laboratories again differ uniformly by this same 20%.

Contrasting with the results from both the photolysis and the LIF measurements for NH_3 collider, however, are findings using a quite different method.[31] Here, the NH was formed from dissociation of NH_3 by a beam of 20 keV electrons, and the time decay of the resulting emission was monitored through a high resolution monochromator. The authors report finding smaller rate constants for lower rotational levels, noting that this is contrary to the results of Hofzumahaus and Stuhl. Many rotational levels are produced in this process although only one fine-structure component of one rotational level was monitored for each decay measurement. Thus, RET by the NH_3 could affect the results, through simultaneous filling and depletion of the level detected. However, RET like quenching proceeds more slowly for higher N', as shown by a comparison of the results of Ref. 24

for N' = 13 ($\sigma_R/\sigma_Q \sim 0.5$) and Ref. 29 for N' = 3 ($\sigma_R > \sigma_Q$), so the reason for this discrepancy is not known.

The cross sections reported in Ref. 25 exhibit acceptably straight lines when plotted in the form ln[σ_Q (N')] vs. N'(N' + 1). From these plots and also an examination of the results for OH, one finds that the more efficient quenchers show a smaller variation with rotational level. An explanation for this is as follows. An especially efficient quencher like polar NH_3 forms strong attractive interactions over the entire potential surface, so the complex can form readily regardless of approach angle. Thus the additional attraction at preferred orientations adds little, and the cross section is not enhanced for rotationless or slowly rotating radicals, as it is in the case of a less efficient collider.

The N'-dependence has also been examined in measurements[32,33] conducted in low-pressure flames of H_2 and hydrocarbons burning in N_2O. Although quite different from discharge flow cell conditions, this is a convenient way to study higher rotational levels. At 14 Torr total pressure, the time decay of LIF following single-level excitation was monitored. The quenching rate was determined from measurements at a fixed pressure by subtracting the known radiative contribution and dividing by the total gas density. The collisional environment where the NH could be found ranged from fuel plus N_2O near 1400 K to H_2O plus N_2 near 2200 K. A decrease in the total quenching rate of about 5% was found when N' was varied from 2 to 12. This result may be due to a small N'-dependence of σ_Q for the species involved (recall that N_2O exhibits none) or a diminished N'-dependence at higher temperature (as seen for OH-H_2O collisions described below).

The rotational level dependence of quenching of the $c^1\Pi$ state of NH has also been investigated. The c-state can be produced by multiphoton photolysis of some precursor or by LIF. In the latter method, excitation is from the metastable $a^1\Delta$ state, formed in turn by photolysis or in a discharge flow system. Rohrer and Stuhl[34] used ArF photolysis of HN_3

to determine cross sections for many collision partners. The nascent, hot c-state distribution was cooled to 300 K by addition of Ar. The cross sections are very close to those for $A^2\Sigma^+$ OH (and quite unlike those for $A^3\Pi_i$ NH) for nearly all the colliders studied. Additionally, ab initio calculations for NH(c)-H_2 collisions[35] show a distinctly anisotropic surface. Thus one might expect a rotational level dependence like that for OH.

Little N'-dependence has been found, however. Intersystem transfer, c→A, was investigated for four colliders both in the absence and presence of added Ar relaxer.[36] O_2 and NO were found to have smaller cross sections for the 300 K rotational distribution than for the hot initial distribution. For O_2, this was attributed to resonant energy exchange involving metastable states of the collider, but no such explanation could be given for NO. Quenching by Xe showed no N'-dependence, while that by N_2O was smaller for the higher N' distribution.

Umemoto et al.[37] made quenching measurements by LIF, exciting single levels of $c^1\Pi$ from the $a^1\Delta$ state, which was produced in the multiphoton XeCl laser photolysis of HN_3. The a-state NH was formed with a large amount of translational energy, equivalent to a temperature of 10500 K; exciting the c-state promptly after the photolysis pulse ensures it has this same high collision velocity. The authors report cross sections for nine colliders, with 1-σ error bars of 17%. No rotational level dependence between N' = 2 and 8 could be discerned within this uncertainty. (The results are compatible with those of Ref. 36 for N_2O, given the error limits in each experiment.) The authors also describe a large series of σ_Q measurements at a translational temperature of 300 K, using He relaxer; however, this produces at the same time a thermal rotational distribution so that N'-specific cross sections could not be determined. Therefore, the lack of an observed N'-dependence in NH ($c^1\Pi$) quenching at high temperature may be inherent to this state, or may reflect a decreased N'-dependence at higher collision energy. In either event, the $c^1\Pi$ state should provide useful comparisons with theoretical models (e.g., Ref. 35 for H_2 collisions). Rotational-level-specific quenching at room temperature, through discharge flow production of $a^1\Delta$ or $b^1\Sigma^+$ and LIF time-decay measurements, is highly deserving of study.

Rotational Level Dependence of Quenching of CH

The rotational dependence of quenching in the CH radical has been investigated very little, although quenching studies have been made on both the $A^2\Delta$ and $B^2\Sigma^-$ states. Each can be produced either by multiphoton photolysis of a suitable precursor or by LIF from the ground $X^2\Pi$ state. In view of the fact that the quenching of CH(A) appears to be governed by repulsive, not attractive, forces (see below), its rotational level dependence is of particular interest.

Nokes and Donovan[38] used multiphoton ArF laser photolysis of acetone and bromoform to produce CH in $A^2\Delta$. A series of colliders was examined using the pressure dependence of the time decay of the emission following the excimer pulse, as in the NH studies described above. Helium was added to produce rotational and translational thermalization in most of the experiments. However, one set of measurements[39] was conducted on quenching by H_2, in the presence and absence of the helium. The hot initial distribution was found to be quenched more slowly than the 300 K distribution.

The rotational level dependence of quenching of both the B and A states was investigated in the same low-pressure hydrocarbon/nitrous oxide flames described above for NH quenching, as well as flames burning in oxygen.[32,40,41] In these experiments the pressures of the flames were varied between 4 and 14 Torr to determine the quenching rate from LIF time decays. Again, the collisional environment is far from fully characterized although the quenching rate was found to vary little with position in the flame (i.e., with temperature and composition). The $A^2\Delta$ quenching rate decreases 9 and 16% when N' increased from 2 to 12 for the fuels C_3H_8 and C_2H_2, respectively. A slightly larger decrease was found for the $B^2\Sigma^-$ quenching rate in each flame. Flames burning CH_4

showed no N'-dependence. Earlier steady-state fluorescence intensity measurements[42] in atmospheric pressure flames had indicated a decrease in σ_Q with N', whereas no N' dependence was discerned for VET or B→A transfer.

KrF laser photolysis of acetone was also used to generate and measure the quenching of CH ($A^2\Delta$) by that same parent molecule.[43] Rotationally resolved emission spectra indicated a distribution over vibrational and rotational levels of $A^2\Delta$ and an approximately equal amount of $B^2\Sigma^-$. The R-branch lines show a smoothly decreasing σ_Q between N'=4 and 8, and the Q-branch, which also includes N'=2 and 3, a somewhat larger value. Although the overlap of emission from the (1,1) and (0,0) bands in both branches and the possibility of B→A transfer complicates the interpretation in terms of A-state quenching alone, there appears a definite dependence on rotational level.

Other Diatomic Hydrides

To our knowledge, in only three other cases involving diatomic hyrides has the rotational level dependence of quenching been considered. Nedelec and coworkers have studied quenching and RET in a large number of metal hydrides, using spectrally and time-resolved LIF in hot discharge cells. The species have included BH, NaH, KH, AlH, CdH, MgH,.ZnH and HgH. Only for the $A^1\Sigma^+$ of the NaH molecule[44] was any rotational effect on quenching investigated. The authors made measurements with H_2 collider on N'=6 and 12 in v'=11, and report that σ_Q "did not depend appreciably" on rotational level. The RET cross sections are similar to those for quenching, not only for this molecule but also[45] for KH($A^1\Sigma^+$). Thus, if a rotational level dependence exists, perhaps for other v' or another collision partner, it should be observable. This could be very interesting in that these pseudo-two-electron molecules may be amenable to simple theoretical treatment.

LIF time decay measurements have also been performed on quenching of the $A^2\Sigma^+$ state of the LiH molecule.[46] The collider was Li, present in the heat pipe used for formation of the hydride. The rotational level dependence of σ_Q in the v'=5 and 6 levels which were investigated is quite marked, owing to sharp resonant transfer producing Li atoms in the 2^2P level and not the type of collision dynamics postulated for OH, NH and CH. However, the theoretical tractability of this small species makes it a most attractive candidate for further study in other v' and with other collision partners.

The $B^2\Sigma^+$ state of the OH molecule can be made to fluoresce[47] using laser excitation from high lying levels of the ground state, for example v" = 8 or 9 produced in a discharge system by the $H+O_3$ reaction. Collisional removal of the excited state by Ar and He varies markedly with N', but this has been attributed to rotational transfer into and out of rotational levels which rapidly predissociate.

Rotational and Temperature Dependence of Quenching of OH by H_2O

Quenching of $A^2\Sigma^+$ OH by the water molecule is an important subject for study from a practical standpoint, i.e., quantum yields in combustion and atmospheric processes, as well as for fundamental reasons. Considering only LIF experiments with single-level excitation made on N'=0, one finds one pair of measurements[3,11] reporting σ_Q=65 Å^2 and another pair[16,48] where a value of 90 Å^2 was found. The pressure of H_2O is notoriously difficult to control and measure accurately in flow systems, so values this diverse are not surprising.

Cleveland and Wiesenfeld[48] photolyzed O_3 to product $O(^1D)$ atoms which react with H_2O to produce OH in high rotational levels of both v" = 0 and 1 of $X^2\Pi_i$. A tunable laser was then used to excite the OH to specific N' of both v' = 0 and 1 in the A-state; time decay measurements as a function of H_2O density furnished σ_Q for each vibrational level (recall that for H_2O, $\sigma_Q \sim 10\sigma_V$). The results agree excellently with those of Refs. 13, 16, and 17, which were made between N' = 0 and 7. These measurements continue to much higher N', showing a further drop in σ_Q to N' = 12 and then a constant value up to

N' = 19. This is very much like the behavior of σ_V at high N' for H_2 and N_2 colliders (see Fig. 1). Apparently, for sufficiently fast rotation the averaging of the surface becomes complete, and a further increase in N' causes no further decrease in efficiency.

Unfortunately, the OH translational energy in this experiment is not known accurately. The $O(^1D)+H_2O$ reaction forms OH with an effective translational temperature[49] of 3500K. The quenching measurements were performed with 1.25 Torr added He, 2 μs after the photolysis laser. At this delay, 8 Torr He thermalizes low rotational levels[50] and surely translation too, but the effects for higher N" and at the lower pressure were not measured directly.

Quenching of OH has also been investigated[51,52] in low-pressure flames of H_2 burning in mixtures of O_2 and N_2O. The method, as for NH in flames, was LIF time decay at a fixed pressure (here 7 Torr) with subtraction of the radiative component. In the reaction zone[51] a noticeable dependence of the quenching rate on N' was found. The degree varied with position and thus with collider and temperature in this complicated environment. In the burnt gases,[52] the use of mixtures of the two oxidants permitted the temperature to be adjusted between 1200 and 2300 K. The σ_Q for three N' from this experiment are shown in Fig. 5. Also included are the H_2O quenching results of Cleveland and Wiesenfeld, assuming a 300 K translational temperature for their measurements. Because the gas composition in the flames varies along with the temperature, a flame chemistry model is needed for interpretation, and even then ambiguities remain. However, three important conclusions can be drawn. First, the average σ_Q for H_2O decreases between 300 and 2300 K; second, quenching by H atoms is significant, with an average $\sigma_Q = 16$ Å^2 at 1200 K. Finally, the magnitude of the N'-dependence for H_2O quenching diminishes with increasing temperature: at 300K, $\sigma_Q(N'=3)/\sigma_Q(N'=16)=1.7\pm0.2$ while at 2300 K the ratio is 1.02 ± 0.04.

This variation is consistent with our hypotheses about the collision dynamics. The σ_Q for each N' should decrease with temperature due to the governance by attractive forces (see below). However, that for low N' should decrease faster than for high N'. This is because, at a higher collision velocity, the enhancement due to the preferred orientations is less effective, in the same way that it is inhibited by faster rotation.

A separate measurement[53] of the N'-dependence of quenching of OH by H_2O is in conspicuous disagreement with the results of Cleveland and Wiesenfeld (see Fig. 3 of Ref. 48) and the mechanistic interpretation above. Multiphoton photolysis of H_2O at 248 nm produced $A^2\Sigma^+$ OH, and rotationally resolved emission was monitored. Time decay as a functios of pressure was used to obtain σ_Q for N'=6 to 17. The results show nearly constant σ_Q, within quoted error bars, for H_2O, N_2 and CO colliders, although the authors suggest that for H_2O there is a significant increase with N' for high N'.

Temperature Dependence of Quenching in OH

Collisional processes governed by attractive forces and complex formation have cross sections which decrease with increasing approach velocity. In contrast, when a potential barrier or repulsive wall dominates, the cross section will increase. Therefore a determination of the velocity or temperature dependence provides important evidence regarding the nature of these intermolecular forces.

This connection, which had been considered for quenching of glyoxal,[18,54] was the motivation for the initial measurements of σ_Q for OH $A^2\Sigma^+$ at elevated temperatures.[4] These were performed in a laser pyrolysis/laser fluorescence (LP/LF) system[55]. A mixture containing SF_6, H_2O_2 and the collider was irradiated with a pulsed CO_2 laser. The infrared radiation is absorbed by the SF_6 and rapidly thermalized, thereby flash heating the system to temperatures as high as 1400 K; OH is formed by the pyrolysis of the peroxide. With proper attention to gas dynamic processes following the initial heating, one has a homogeneous sample at high temperature in which to perform quenching studies using the time decay of LIF signals. The SF_6 is (fortunately!) a very inefficient quencher but quite effective at RET. Therefore, the LP/LF results are for a thermal distribution in the excited at the experimental temperature (obtained from excitation scans yielding $T_{rotational}$ in the ground state of the OH), and N'-specific cross sections cannot be determined.

In Ref. 4, σ_Q are reported for eleven quenchers at temperatures near 1100 K; some redeterminations and extensions to larger hydrocarbons are given in Ref. 21. For a proper comparison of these thermally averaged σ_Q with those at lower T, one must consider also the rotational dependence which, however, is known only at 300 K. In Fig. 6, the thermally averaged σ_Q at 1100 to 1200 K, determined by LP/LF, is plotted vs. $\sigma_Q(N'=5)$ measured at room temperature; this is the rotational level most highly populated at the elevated temperature. σ_Q decreases in all cases.

The temperature dependence of quenching was also investigated[56] at lower temperatures, 230 to 310 K, for the colliders H_2, N_2, O_2 and CO_2, by cooling with dry ice the flow cell described earlier. Argon was added at a pressure of 8 to 10 Torr so a thermal excited state rotational distribution was always maintained. σ_Q for NH_3 was measured[57] over this range in the flow cell and also between 800 and 1450 K using the LP/LF system. The results for CO_2 and N_2 (including the other LP/LF results[4,21]) are shown in Fig. 7.

As T increases, the thermally averaged σ_Q decreases due to two effects. First, the attractive nature of the forces causes an inherent decrease for any N'; second, the distribution shifts to higher N' which have lower σ_Q at any T. The lines with long dashes in Fig. 7 show the change from the first cause, calculated using the one-dimensional multipole interaction model. The lines with short dashes show the amount of decrease from the shifting distribution, assuming (perhaps incorrectly, as discussed above) the N'-dependence does not vary with T; the solid lines represent the combined effect. In each case, the calculated values are matched to the experiments at 300K. It appears that, even with these simple ideas, we understand reasonably well the attractive interactions for CO_2 collider. Other gases, save N_2, also fit this picture; see Fig. 6 and Refs. 21, 56 and 57.

N_2 exhibits a much sharper decrease than the other colliders, which can be explained as follows. Nitrogen also quenches anomalously weakly, that is, a complex is formed but the Σ-Π state mixing is not strong for N_2. At low T and thus lower collision energy the complex lives longer, allowing the collider-induced state mixing perturbation to last longer, but there is not enough time to effect sufficient mixing at the higher temperature. That is, for N_2 the probability P for quenching decreases with decreasing complex lifetime and with increasing T. In contrast, CO_2 and other colliders are so efficient that the Σ-Π mixing is complete even for the shortest lived complex, and P is independent of T.

As one approaches much higher collision energies, and less effective quenching due to the attractive force interactions, the repulsive wall of the potential may begin to play a role in the quenching. For such a mechanism, σ_Q will become constant and eventually begin to increase with further increase in T. A constant or nearly constant value of σ_Q at high T is consistent with the combined LP/LF and flame results for H_2O quencher,[52] and an increase is hinted at in quenching by NH_3 at elevated temperature.[57]

The temperature dependence of VET in excited OH (or the other hydrides) has not been investigated. Besides its fundamental interest, it has practical significance for LIF monitoring of OH for both combustion and atmospheric chemistry. From the picture developed thus far, we expect a variation in σ_V similar to that in σ_Q for most colliders. For N_2, where the vibrational state mixing is efficient in contrast to the ineffective electronic state mixing, we anticipate a much smaller temperature variation in σ_V than was found for σ_Q.

Temperature Dependence of Quenching in NH, PH and CH

LIF decay measurements[28] in the LP/LF system were also used to study quenching of the $A^3\Pi_i$ state of NH at 1400 K; the radical was produced by addition of small amounts of NH_3, which reacted with F atoms formed by pyrolysis of the SF_6. The rotational population is thermal, with N' = 5 most highly populated at this temperature, so comparison should be made with the room temperature values of σ_Q for this level.[25] As for OH quenching, NH_3 shows a large decrease, from 80 to 26 $Å^2$. There are also decreases for CH_4, CO and O_2, but CO_2, N_2O and H_2 exhibit no temperature dependence. For H_2O collider, comparison can be made between the room temperature results and the flame measurements[33]: $\sigma_Q(N' = 6)$ at 300 K is about twice the upper limit of 17 $Å^2$ measured at 2300 K. Thus for the colliders which have evident dipole-dipole attractive interactions and large cross sections, increasing the temperature produces a decrease in σ_Q. This is in accord with the picture constructed for OH quenching. For nonpolar colliders, however, the behavior is varied, and the mechanism must involve more than simple complex formation with a constant Π-Σ mixing interaction. This does not invalidate the explanation developed to describe the N'-dependence, however. The initial stage of the collision could still consist of entrance channel dynamics on an anisotropic attractive surface, with the probability P of quenching controlled by subsequent, partner-dependent state mixing within that complex.

Quenching of thermal NH $A^3\Pi_i$ has been studied[26] at 300 and 415 K, for the same set of colliders listed above plus C_2H_6. The excited state was formed by photolysis of NH_3 in the presence of 100 Torr Ar which produces thermalization but not quenching. Between these temperatures σ_Q decreased 10 to 25%, depending on collider, except for CO_2. The shift in rotational distribution between these two temperatures can account for only a 2 to 5% decrease.

The $A^3\Pi_i$ state of the PH radical is similar that of the isovalent NH. It too has been studied[58] at these same temperatures, 300 and 415 K, using 193 nm photolysis of PH_3 in the presence of Ar as the rotational relaxer. Individual σ_Q are similar though not identical to those for NH $A^3\Pi_i$, including small values for both N_2O and CO_2. For other molecules there is a 20 to 30% drop in σ_Q between these two temperatures. N_2 is especially interesting. It did not quench NH (σ_Q<0.006 Å^2) but does quench PH with a small σ_Q of 0.6 Å^2 at 300 K. However, at 415 K, this has dropped to 0.36 Å^2; as for OH, quenching by this inefficient collider exhibits an especially large temperature dependence. One would then expect σ_Q to be much larger at cold temperatures, and also to find a measurable value for NH in a sufficiently cold cell.

The $c^1\Pi$ state of NH has a collider specificity of σ_Q which mimics that of $A^2\Sigma^+$ OH, as noted above, and one might well expect a similar collision energy dependence. Two sets of LIF measurements have been made,[37] one exciting from $a^1\Delta$ at an equivalent translational temperature of 10500 K and the other thermalized at 300 K, using Ar relaxer with a time delay following the photolysis laser. Recall that no rotational level dependence could be discerned at the higher temperature; if true for all T, a direct comparison is possible. For all nine colliders investigated, σ_Q was smaller at the higher energy; the amount of decrease ranged from 60 to 80%.

The temperature dependence of the quenching of $A^2\Delta$ CH is, however, quite different. Several investigations at different temperatures have included enough common colliders to form comparisons. In those at room temperature, excimer laser photolysis formed the excited state directly, and decay time measurements in the presence of a thermalizing rare gas furnished σ_Q. Results are available from ArF photolysis of acetone[59] and acetone or bromoform,[38] and KrF photolysis[60] of CH_2Br_2. The results from these three studies, tabulated in Ref. 60, spread over about a factor of two for common colliders; this is nonetheless suitable for an examination of the temperature dependence. Excimer laser dissociation of acetone and thermalization by Ar was also used[61] to measure σ_Q for several colliders at the elevated temperature of 415 K.

Quenching of this state has also been studied at higher temperature. The LP/LF method[62] was used for measurements at 1300 K, producing the radical by the reaction of added CH_4 with F atoms formed in the SF_6 pyrolysis. In addition, upper limits for σ_Q have been obtained near 1800 K in the low pressure flame system[32,41] for H_2O, N_2 and CO_2 (these replace earlier values[40] where the ability to obtain only limits from these flames had not been recognized).

Altogether, one has cross sections at different temperatures available for those three colliders and for H_2, O_2, CO, N_2O and NH_3. For polar NH_3, σ_Q decreases slightly between 300 and 415 K, and 30% further by 1300 K. The temperature dependence of σ_Q for CO, O_2 and H_2O is ambiguous; possible differences are smaller than error bars and the interpretation depends on the choice of σ_Q at 300 K from among Refs. 38, 59 or 60. The other four colliders, however, show an increase in σ_Q as the temperature increases. The changes are dramatic: σ_Q doubles between 300 and 415 K and increases another factor of five to twenty, depending on collider, going to 1300 K. The cross section limits at 1800 K are yet higher. This behavior is that expected for a collision governed by a potential barrier or repulsive wall. Assuming that a barrier is responsible, its height may be obtained through an Arrhenius plot; the results of such an analysis[61] show activation energies ranging from 2 to 4 kcal/mole.

The temperature dependence for $A^2\Delta$ CH is thus very different from that of the other radicals. For all colliders investigated, OH $A^2\Sigma^+$ and $c^1\Pi$ NH show a decrease in σ_Q with increasing T, and a decrease is found in most cases for quenching the $A^3\Pi_i$ states of both NH and PH. This indication of the role of attractive forces makes sense, at least for the A states of OH and NH, in view of their dipole moments, 2.0 and 1.3D, respectively.

However, the A state of CH has a comparable dipole moment of 0.9D. Thus, if a mechanism involving long range attractive forces and complex formation is responsible for quenching of the other radicals, a simple view would suggest it should be for CH as well. This appears true for the polar collider NH_3 but not H_2O, while in most other cases the quenching seems to be governed by a barrier, even though the cross sections are fairly large, a few Å^2. Therefore the collision must involve more complicated interactions than only long range attractive forces. We do know that such an extension of these simple collision complex ideas breaks down in another case for these same species, the comparison of VET in the excited and ground[63] electronic states of OH. For the polar colliders NH_3 and H_2O, σ_V for the $X^2\Pi_i$ and $A^2\Sigma^+$ states are quite similar. However, for other colliders, VET proceeds a hundred to a thousand times more slowly in the ground state. Both states have comparable dipole moments (that of the X state is 1.7D) so in this case more than just the long range part of the potential must be involved.

Recall that, like NH and OH, CH exhibited a decrease in σ_Q with increasing N'. Therefore, it appears that in CH the surface is also anisotropic. Perhaps a complex is indeed involved, with entrance channel dynamics controlling its formation, but if so, then the Δ-Π state mixing within the complex must be governed by some repulsive interaction occurring on a different region of the potential surface.

Summary

We have reviewed experiments investigating the rotational level and translational energy dependence of collisions of electronically excited states of simple diatomic hydrides. For processes of quenching and VET that proceed more rapidly than rotational thermalization, the cross section decreases with increasing N', suggesting an anisotropic potential surface. For $A^2\Sigma^+$ OH, there exists considerable evidence suggesting the role of long range attractive forces, including a decrease in σ_Q with increasing temperature, and it appears that collisions of this molecule are relatively well described by such a simple picture. For NH and CH matters are more complex. The N' dependence again suggests orientational effects but the variation with temperature is not uniform and clearly indicates repulsive forces for CH. Such variations in behavior among otherwise similar radicals, between two excited states of the same radical (NH), and for various collision partners are not simply explained. They should therefore provide good tests of more detailed theoretical treatments of the collisions of these small, computationally tractable species. Several useful future experiments are immediately evident, such as the N' dependence of quenching of NH ($c^1\Pi$) at room temperature and the temperature dependence of VET in OH ($A^2\Sigma^+$). As more information becomes available, these unusual effects in these interesting excited diatomic hydride species should continue to enhance our knowledge of molecular collision dynamics.

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Figure Captions

Figure 1. Fluorescence scan in the presence of 1 Torr H_2 collider, exciting the N'=3, J'=$3\frac{1}{2}$ level of the v'=1 vibrational level in $A^2\Sigma^+$ OH. Emission to the right of 3120 Å is the (1,1) band, and consists mostly of five strong lines originating from the intially pumped rotational level, showing that little RET has occurred. Fluorescence at shorter wavelengths is the (0,0) band, emitted by OH molecules which have undergone VET from v'=1 to 0. Comparison of the intensities shows that more VET has taken place than RET in v'=1.

Figure 2. Cross sections for VET due to H_2 and N_2. The logarithm of σ_V is plotted vs. N'(N'+1), i.e., the rotational energy. This empirical correlation appears to work well for lower rotational levels but not higher, as shown by the lines.

Figure 3. Decay constants for v'=0, plotted vs. pressure of added CO_2 collider, for several rotational levels of OH (upper panel) and OD (lower panel). The rate constant for quenching is obtained from the slope, and the intercept is the radiative rate. Note the striking variation of slope with N'.

Figure 4. Cross sections for quenching v'=0, plotted in logarithmic form vs. the rotational energy, for OH and OD with the two colliders N_2O and CO_2. Both isotopes fit on the same curves when plotted in this way.

Figure 5. N'-dependent quenching rate constants for v'=0 over a large temperature range. Squares: N'=3; circles: N'=8; triangles: N'=16. The points at 300 K are for H_2O collider, from Ref. 48. Those at higher temperature are from flame studies, Ref. 52. At the highest temperatures the quenching is due to

H_2O, although hydrogen atoms contribute significantly at 1200 K. Comparing the points at highest and lowest temperature shows that the rotational level dependence present at 300 K has disappeared at 2300 K.

Figure 6. Cross sections for quenching of v'=0, showing a decrease with temperature for the eleven colliders studied at 300 K (Ref. 17) and elevated temperature, 1100 to 1200 K (Refs. 4 and 21). The room temperature value for N'=5 is plotted to minimize effects due to the rotational dependence; at 1200 K, the most probable value of N' is 4.5.

Figure 7. Experimental and calculated temperature dependence of quenching cross sections for v'=0 for collisions with CO_2 (upper panel) and N_2 (lower panel). Triangles: Ref. 4; open squares: Ref. 21; circles: 300K thermal average calculated from the results of Ref. 17; filled squares: Ref. 56. The calculated temperature dependence arising from the shift in the N'-distribution together with the N'-dependence of σ_Q at 300K is given by the short dashes. The calculated temperature dependence predicted by the multipole interaction model is shown by the long dashes. The solid line exhibits the combination of the both effects.

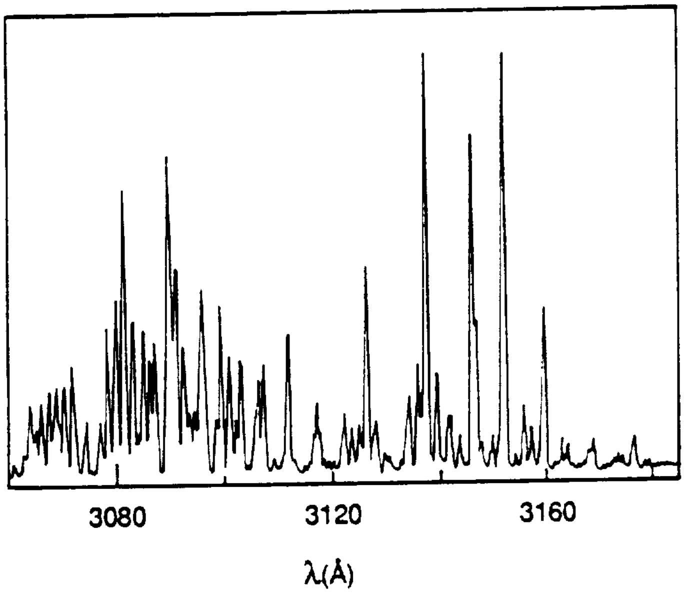

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Figure 1

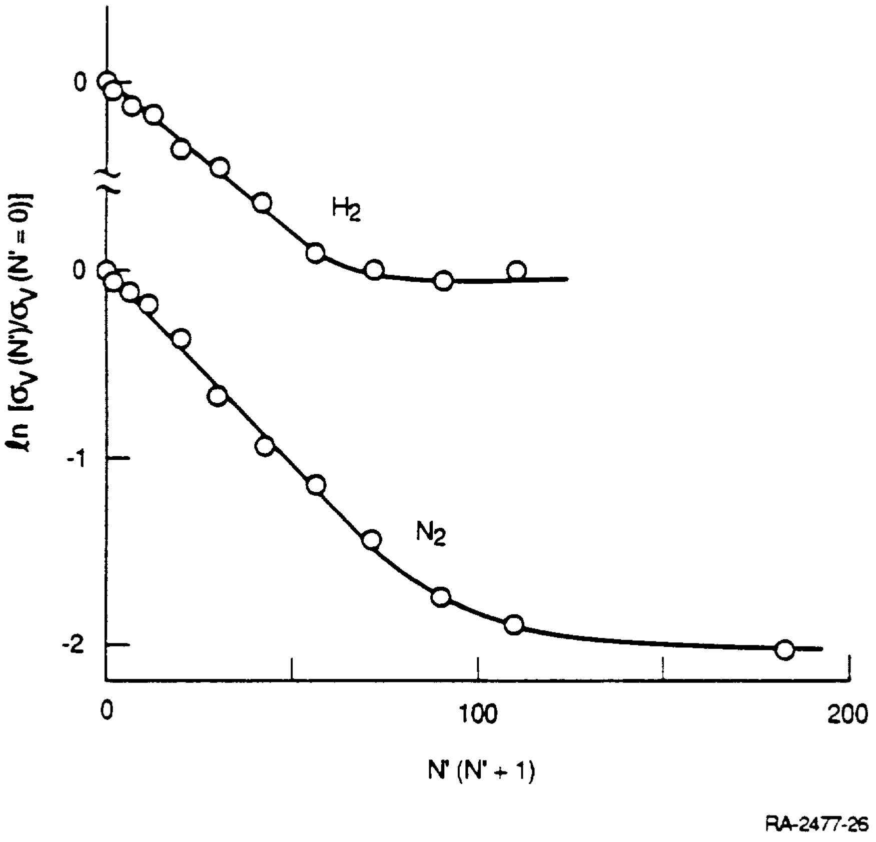

Figure 2

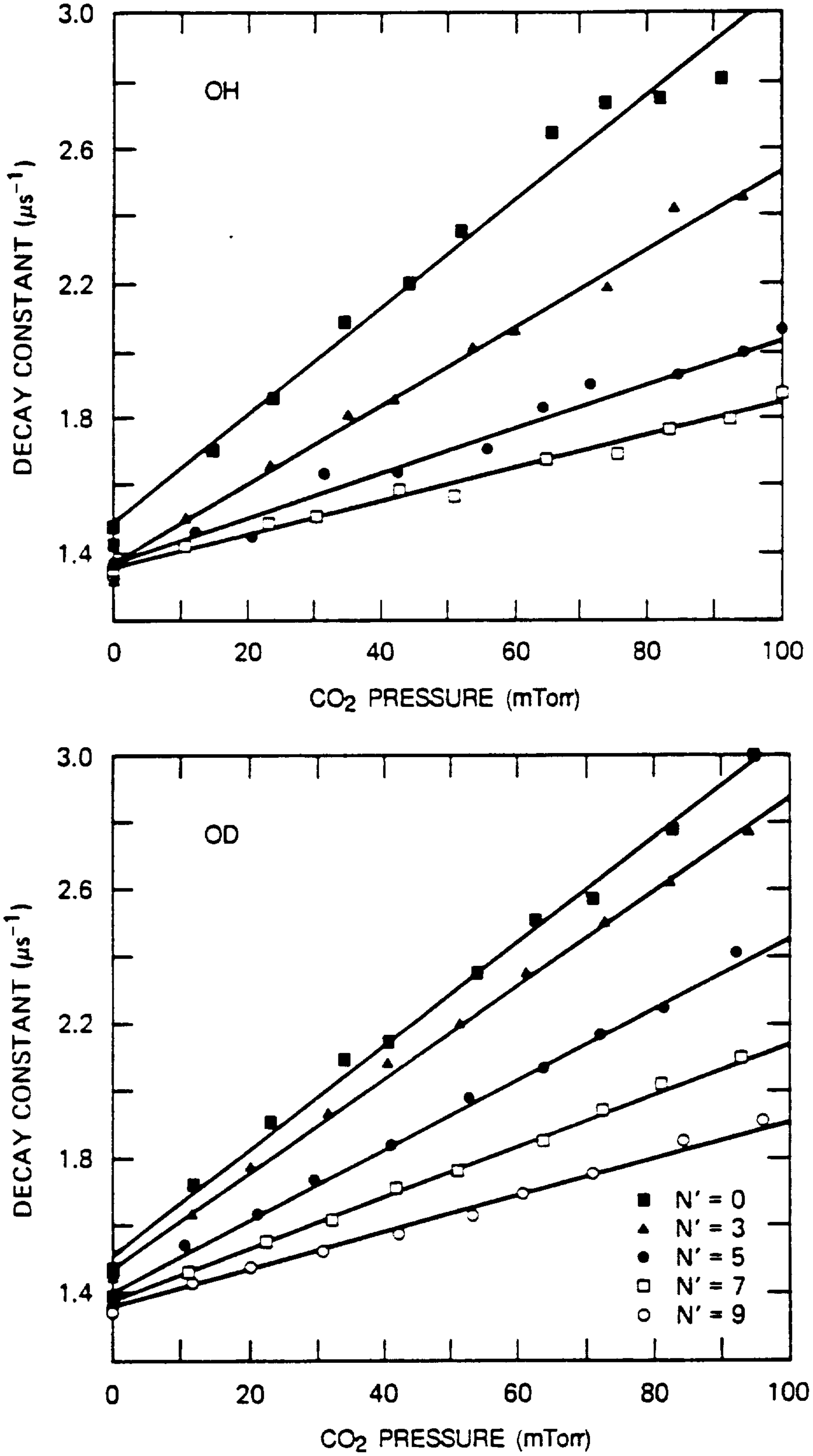

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Figure 3

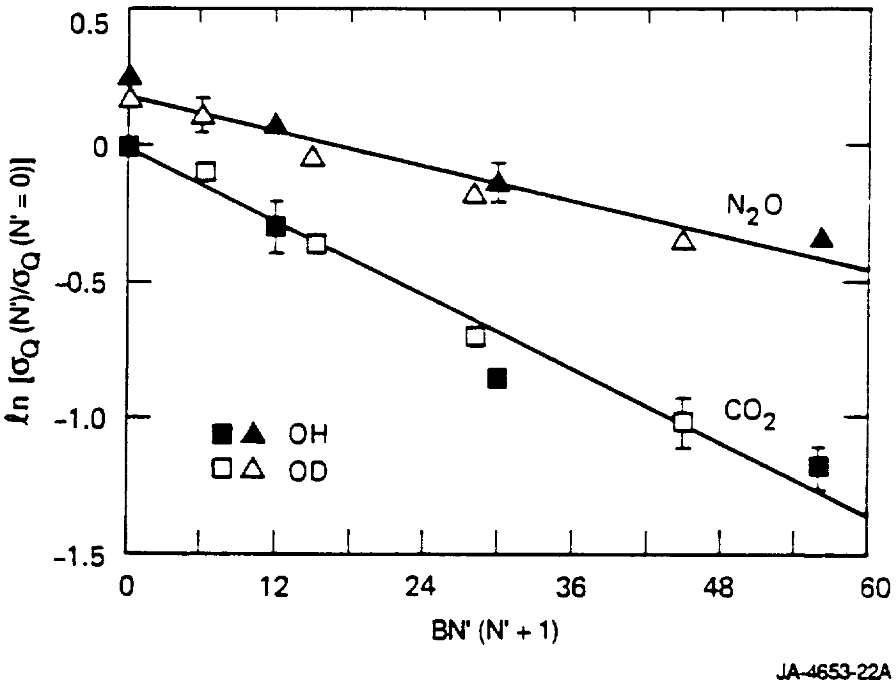
0.5
0
-0.5
-1.0
-1.5
$\ell n\ [\sigma_Q(N')/\sigma_Q(N'=0)]$
0
12
24
36
48
60
BN' (N' + 1)
N_2O
CO_2
■ ▲ OH
□ △ OD
JA-4653-22A

Figure 4

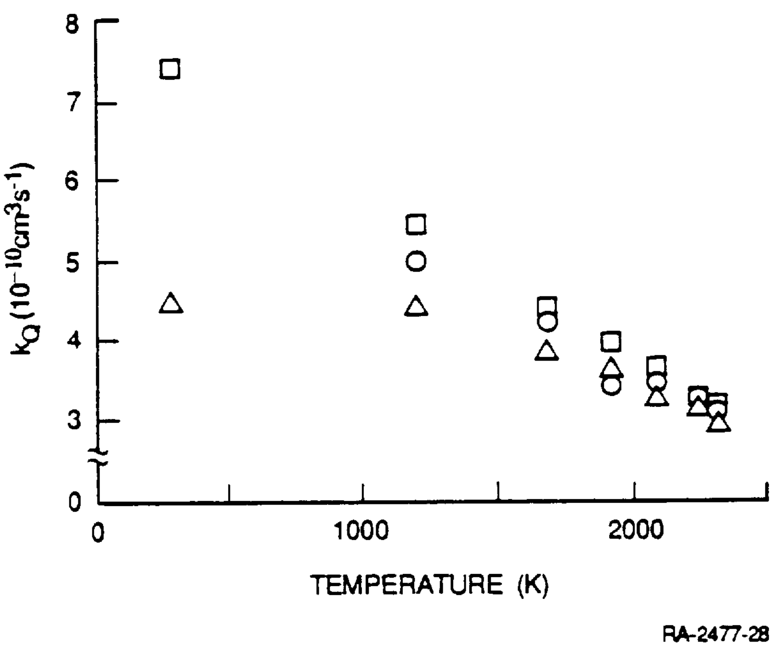

Figure 5

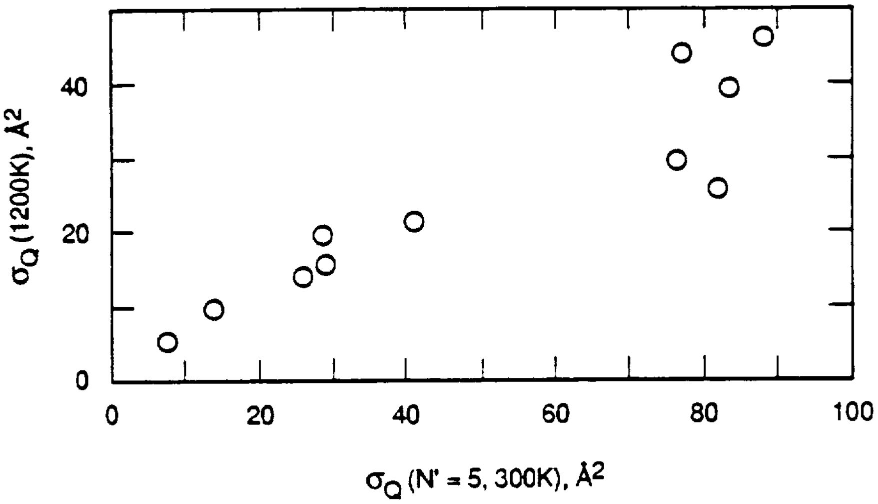

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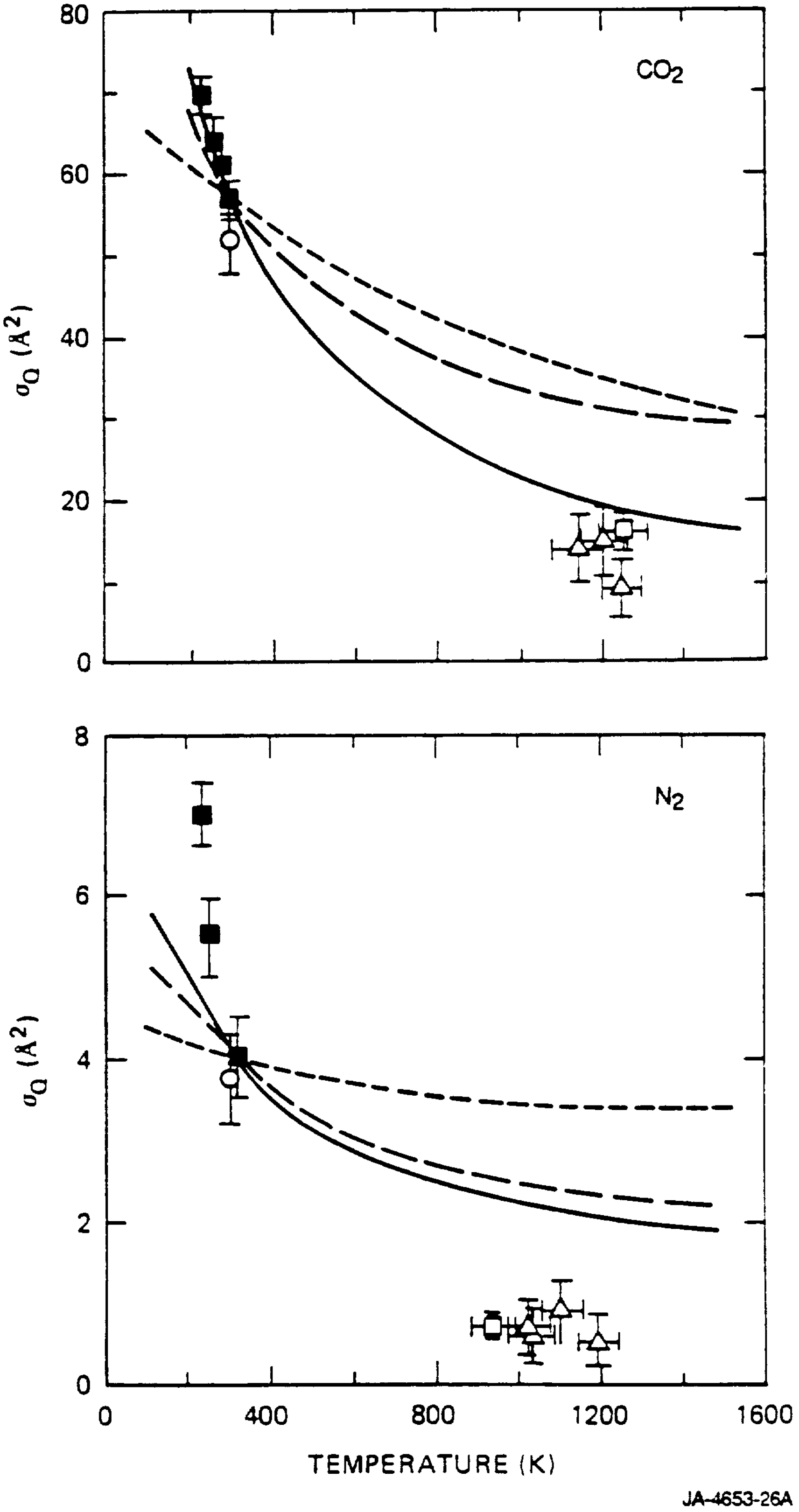
Figure 6



80
60
40
20
0
σ_Q ($Å^2$)
CO_2
8
6
4
2
0
σ_Q ($Å^2$)
N_2
0
400
800
1200
1600
TEMPERATURE (K)
JA-4653-26A

Figure 7