

# QUENCHING REACTIONS OF ELECTRONICALLY EXCITED ATOMS

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## Abstract

The two-body, thermal quenching reactions of electronically excited atoms are reviewed using excited states of Ar, Kr, and Xe atoms as examples. State-specific interstate relaxation and excitation-transfer reactions with atomic colliders are discussed first. These results then are used to discuss quenching reactions of excited-state atoms with diatomic and polyatomic molecules, the latter have large cross sections, and the reactions can proceed by excitation transfer and by reactive quenching. Excited states of molecules are not considered; however, a table of quenching rate constants is given for six excited-state molecules in an appendix.

## 1 Introduction

Collisions of electrons with atoms and molecules can produce electronic excitation. At least for atoms, such excitation is frequently to states of higher energy than those derived from the valence electron shell (with principal quantum number =  $n$ ). Excitation to levels with principal quantum numbers of  $n+1$ ,  $n+2$ , etc. alters the intrinsic chemical nature of the excited atoms relative to the reactivity conventionally associated with ground state atoms of that element. For example, the reactivity of the  $np^5(n+1)s$  or  $p$  states of the rare gases have chemical properties closely associated with those of alkali metal atoms, because of the similarity of their ionization energies. These low ionization energies introduce attractive ion-pair interaction potentials arising as a consequence of charge transfer from the excited state atom to collider molecules with positive electron affinities. Of course, this is the basis of the rare gas halide systems, which provide the excimer laser. The low ionization energies of excited-state atoms of even non-metallic elements mean that these states have chemical properties normally associated with metal atoms, but with non-filled ion-cores. Some authors have used the term "super alkali" to describe the chemical properties of excited states of the alkali metals. In addition to coulombic interaction potentials, attractive covalent interactions also can exist, especially between the excited-state atom and a collider atom or molecule with open-shell structures, i.e., those with unpaired electrons. These covalent interactions can be with the excited outer electron or with the unfilled ion-core of the excited atoms. For example, the rare gas  $np^5(n+1)s$  atoms form bound dimer molecules with their own ground state atoms with dissociation energies of  $\sim 1$  eV. These attractive interaction potentials between the excited atom and a collider can open excitation-transfer exit channels with large energy defects or lead to actual chemical reaction. Since the ground-state atoms of most elements are reactive, one can expect enhanced (as well as different) reactivity for their electronically excited-state atoms, even for collisions at room temperature.

Another common feature of excited-state atoms is the presence of a large number of excited states of similar energy corresponding to different values of the various quantum numbers. Collisions with an inert buffer gas, such as He, Ne and Ar, can mix populations in states of similar energy. Such processes sometimes are called fine-structure changing collisions or inter- and intra-multiplet transfer processes. If the electronic energy is sufficiently high, energy transfer to the target atom or molecule also may occur. Thus, collisional quenching of a given excited state of an atom frequently has several possible product states (often called exit channels). The variety of exit channels means that total quenching rate constants are usually better characterized than are the product states.

Collisional quenching of excited-state atoms are non-adiabatic processes, i.e., the description of the potential energy surface changes during the course of the collision, since the entrance and exit channels are different electronic states. Thus, statistical theories of rates of chemical reactions are not applicable. In principle, these quenching reactions can be described by evaluating the equations of motion along the potential curve or surface with consideration of the probability of transfer from entrance to exit channels. However, the number of potentials in a given collision process can be large, and the accuracy required to obtain rate constants that are satisfactory for laboratory work make this first-principle approach impractical, unless a very detailed understanding is desired for a specific reaction. Nevertheless, a qualitative understanding of interaction potentials is required to provide a framework for models of the quenching processes. Unless the exit channel is endoergic or the crossing between entrance and exit channel occurs on the repulsive wall of the entrance channel

potential, quenching reactions usually have modest temperature coefficients [1].

For the same reagent molecule, the quenching rate constants will generally increase with electronic energy of the atom. If the excitation energy exceeds the ionization energy of the target molecule, then Penning ionization becomes another product channel. In a few cases, chem-ionization channels may have to be considered. If the quenching occurs from a repulsive entrance channel potential, the ionization cross sections can be smaller than for other competing quenching processes for polyatomic molecules. Theoretical models for Penning ionization processes that occur from repulsive entrance channel potentials are realistic enough to be useful [2]. If the entrance channel potential is attractive, the description for Penning ionization becomes more complicated.

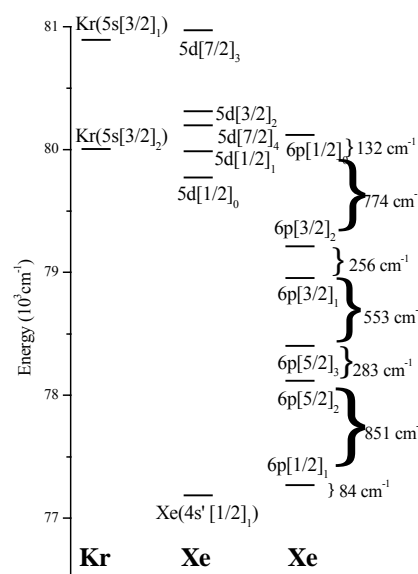
In this paper, different categories of quenching reactions will be surveyed from an empirical viewpoint. The survey will begin with quenching processes that have characteristically small rate constants  $k(T)$ ,  $1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , which corresponds to thermally averaged cross sections,  $k(T)/\langle v \rangle$ , of  $\sim 1\text{-}2 \text{ \AA}^2$ , and continues to those reactions with much larger rate constants  $\leq 200 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ \AA}^2$ . A more or less equivalent statement is that the survey proceeds from collision-induced interstate relaxation processes, to collisional excitation-transfer processes with atomic and diatomic molecular targets, and finally to quenching processes by polyatomic molecules. Most examples will be taken from the extensive room temperature data for states of Xe, as well as from a recent study by Sadeghi and co-workers on reactions of the Ar ( $3p^5 4p$ ) atoms [3]. This choice constrains the range of electronic energy to 8.3-13 eV. An extensive body of literature also exists for interstate relaxation of excited states of alkali and alkaline earth metal atoms. But these elements presumably are of less interest to those investigators who study high-pressure plasmas.

The quenching reactions of electronically excited molecules differs from those of atoms because, for the most part, only excited valence or mixed valence-Rydberg states of molecules are strongly bound. Thus, the excitation energies for molecules generally are lower than for the atomic states mentioned above. Except for the lowest energy excited state, quenching of molecules proceeds by internal relaxation to a nearby electronic state, by excitation transfer to the collider, or by chemical reaction with the collider. The first excited state for some molecules, such as the  $a^1$  states from  $\Phi^2 B^4 B^{*2}$  configuration of molecules isoelectronic with  $O_2$  and the  $N_2(A^3 \Gamma_u^+)$  state, have small quenching constants, except for colliders that can react by excitation transfer. Most other excited molecular states are easily quenched, although each molecule tends to have its own special features, including a particular radiative lifetime. No attempt will be made to provide a summary of reactions of excited-state molecules other than to show a table of 300K rate constants for six molecular states with common collider molecules as an appendix. By coincidence, these six molecules have rather large quenching constants. Just as for the reactions of excited-state atoms, more is known about quenching rate constants than about the product states in quenching reactions of electronically excited molecules.

## 2 Interstate Relaxation of Xe( $5p^5 6p$ ) and Ar( $4p^5 4p$ ) Atoms

Because of interest in the Xe atomic laser, the collisional interstate relaxation among the six states in the Xe ( $6p$ ) and Xe ( $6s'$ ) manifold have been characterized experimentally [4] and studied theoretically [5]. The relevant Xe energy levels are shown in the diagram to the right; the prime denotes states with the  $Xe^+(^2P_{1/2})$  core. The absolute energy of the  $6s'[1/2]_1$  level is 9.57 eV; only three lower energy levels exist:  $6s'[1/2]_0$  -9.45,  $6s[3/2]_1$  -8.44 and  $6s[3/2]_2$  -8.32 eV. The different energy defects between the states, the range of values for the total angular momentum, and the presence of the  $5d[1/2]_{0,1}$  and Xe ( $4s'[1/2]_{1,0}$ ) levels make this an illustrative manifold of levels to examine. The approach of the rare gas atom collider to the  $Xe^*$  atoms will give "diatomic" potentials with characteristic  $\Omega$  values ranging from 0 to J for each state. The attractive nature of these potentials increases from He to Xe as colliders. Total quenching constants and product branching fractions have been reported for collisions with all the rare gas atoms [4]. The results, as thermal average cross sections and product branching fractions, are summarized in Table I for He, Ne, Ar and Xe as colliders.

Table 1. Cross-sections and product branching fractions for interstate relaxation of Xe ( $6p$ ) states<sup>a,b</sup>



Xe (6p) State	He	Ne	Ar	Xe
6p[1/2] <sub>0</sub> Ψ	1.6	5.7	37	1.8
5d[1/2] <sub>1,0</sub>		1.0	0.71	c
6p[3/2] <sub>2</sub>	1.0		0.29	c
6p[3/2] <sub>2</sub> Ψ	0.13	0.06	8.9	28
6p[3/2] <sub>1</sub>	0.64	0.21	0.03	0.13
6p[5/2] <sub>3</sub>	~0.35	~0.15	~0.01	0.33
6p[5/2] <sub>2</sub>		~0.15	0.14	0.32
6p[1/2] <sub>1</sub>			0.03	<0.01
6s'[1/2] <sub>1</sub>		~0.15	0.65	<0.01
6s'[1/2] <sub>1</sub>		~0.15	~0.02	0.22
6p[3/2] <sub>1</sub> Ψ	5.8	0.07	0.44	37
6p[5/2] <sub>3</sub>	0.98	0.40	0.15	0.83
6p[5/2] <sub>2</sub>			~0.05	0.10
6p[1/2] <sub>1</sub>		~0.06	0.32	0.02
6s'[1/2] <sub>1</sub>		~0.06	~0.20	
6s'[1/2] <sub>0</sub>		0.42		
6p[5/2] <sub>3</sub> Ψ	0.6	0.55	6.7	18
6p[5/2] <sub>2</sub>	0.7	0.43	0.39	0.45
6p[1/2] <sub>1</sub>		0.59	0.59	0.23
6s'[1/2] <sub>1</sub>				0.10
6s'[1/2] <sub>0</sub>				0.17
6p[5/2] <sub>2</sub> Ψ	0.74	0.95	18	33
6p[1/2] <sub>1</sub>	0.53	0.93	0.72	0.38
6s'[1/2] <sub>1</sub>	0.21	0.02	0.19	0.16
6s'[1/2] <sub>0</sub>				0.38
6p[1/2] <sub>1</sub> Ψ	~2.3	0.06	1.6	45
6s'[1/2] <sub>1</sub>	1.0	0.57	~0.5	0.55
6s'[1/2] <sub>0</sub>		~0.01	~0.2	0.33

- These data were taken from reference [4] or from studies quoted in this summary paper.
- Total quenching cross-sections in Å<sup>2</sup> are given in the first line for 300 K conditions. Branching fractions  $k_{ij}/k_Q$  are given under each cross section, and they may sum to less than 1.0, because endoergic processes are not listed, 6s[3/2]<sub>2,1</sub> states can be products, and experimental uncertainty in the  $k_{ij}$ .
- These branching factors have not been assigned because the high pressures required for quenching of Xe (6p[1/2]<sub>0</sub>) lead to relaxation of the product states.

The majority of the relaxation process can be understood as transfer from one Xe\* state to another when diabatic

potentials of the same  $\Omega$  symmetry originating from different asymptotic states cross with the probability for transfer from entrance to exit channels given by a Landau-Zener type formulation. In a few cases, rotational coupling between potentials differing by  $\Delta\Omega = \pm 1$  may be important. The calculated potentials for the interaction of He and Ar atoms with Xe (6p and 6s') states plus close-coupled calculations on these potentials show that this model is realistic [5]. For a few cases, spectroscopic data [6,7] are available for some of the Xe (6p)-Rg potentials and more quantitative models now could be developed.

Except possibly for Ne buffer gas, the cross sections are sufficiently large that the populations in the Xe (6p) states will relax to the Xe (6s) levels at modest pressures of He, Ar or Xe. The total quenching cross sections and the product branching fractions show differences with respect to the Xe (6p) states for a common collider and with respect to He, Ne, Ar and Xe as colliders for a common Xe (6p) state. The pattern is complicated, especially for the  $6p[1/2]_0$  level, perhaps because it has a single potential with  $\Omega = 0^+$ . Also the Xe (5d) levels cannot be observed directly, and their branching fractions were assigned indirectly. These data show that the cross sections do not follow simple energy defect arguments. However, a few trends can be noted.

- i. The total cross-sections for Xe are in the range of 20-40  $\text{\AA}^2$ , except for the  $6p[1/2]_0$  state, and the distribution of product states is broad. The latter is a consequence of the bound nature of several potentials correlating to these Xe (6p) levels. On the other hand, the single  $\Omega = 0^+$  potential from the Xe ( $6p[1/2]_0$ ) state is repulsive and the interaction with exit channels is weak.
- ii. Quenching by Ar has variable cross sections, and usually several exit channels are important. This is related to the attractive nature of a few of the Xe (6p) – Ar potentials. The large cross section for  $6p[3/2]_2$  with formation of mainly  $6s'[1/2]_1$  with an energy defect of 0.25 eV was reproduced by the calculations [5]. The explanation is two curve crossings in sequence with  $\Omega = 0^+$  symmetry, i.e.,  $6p[1/2]_1 \rightarrow 6p[5/2]_2 \rightarrow 6s'[1/2]_1$ . The surprisingly large cross section for  $6p[1/2]_0$  mainly is a consequence of coupling to  $5d[1/2]_1$ .
- iii. The total cross sections for Ne are  $< 1 \text{\AA}^2$ , except for  $6p[1/2]_0$ , which couples readily to the  $5d[1/2]_1$  state. Although the energy defect is only  $84 \text{ cm}^{-1}$ , the cross section for transfer from  $6p[1/2]_1$  to  $6s'[1/2]_1$  is very small, as are the cross sections for the  $6p[3/2]_{2,1}$  states. The branching fractions for the formation of  $6p[1/2]_1$  and  $6p[5/2]_2$  from quenching of  $[5/2]_3$  are nearly equal, in spite of the large difference in energy defect.
- iv. Quenching by He has variable cross sections but exit channels with small energy defects are favored, except for  $6p[1/2]_0$ . The general pattern for the cross sections seems to be matched by the calculations [5]. In particular, the large cross section for  $6p[3/2]_1$  with formation of  $6p[5/2]_3$  is reproduced and the reason is identified as the interaction of 0 potentials. Quenching of  $6p[1/2]_0$  gives  $6p[3/2]_1$  and not  $5d[1/2]_1$ ; the theoretical calculations [5] obtained about the right cross section, but for the wrong product state.

The quenching of Xe ( $6p[1/2]_0$ ) atoms by Kr is an interesting case [8]. The cross section is  $31 \text{\AA}^2$  and the product is  $\sim 90\%$  Kr ( $5s[3/2]_2$ ). The interstate transfer cross sections for Kr with the lower Xe (6p) states are 3-4 times smaller. In a subsequent collision with Xe, the Kr ( $5s[3/2]_2$ ) atom transfers energy back to the Xe (6p) manifold with a cross section of  $46 \text{\AA}^2$  [8,9]. The interstate relaxation cross sections of the lower Xe (5p) states by Kr are as expected relative to Ar or Xe. However, the explanation of how the Xe ( $6p[1/2]_0$ ) state selectively couples to the Kr( $5s[3/2]_2$ ) exit channel and bypasses the many Xe\*-Kr potentials in the same energy region remains to be found.

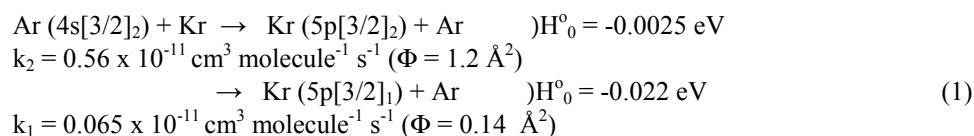
The interstate relaxation cross sections of Ar ( $4p'[1/2]_0$ ,  $4p[1/2]_0$ ,  $4p[3/2]_2$  and  $4p[5/2]_2$ ), which span the 13.48-13.09 eV energy range, have been studied in He, Ne and Ar [3]. The four cross sections with Ar are similar,  $\sim 2.5 \text{\AA}^2$ , and a broad distribution of Ar ( $4p, 4s', 4s$ ) products are formed because of the presence of Ar ( $4p$ )-Ar bound potentials. The cross sections for He and Ne with Ar ( $4p'[1/2]_0$ ) are surprisingly small ( $\sim 0.02 \text{\AA}^2$ ), presumably because the energy defect for the nearest energy Ar ( $4p'$ ) level is 0.12 eV. The cross sections for the three Ar ( $4p$ ) states are  $\sim 1 \text{\AA}^2$  in He, but only  $0.2 \text{\AA}^2$  in Ne. Thus, interstate mixing cross sections are smallest for Ne as a collider gas for both Xe (6p) and Ar ( $4p', 4p$ ) states. The cross sections for quenching of Ar ( $4p', 4p$ ) atoms by Kr and Xe increase to 30-100  $\text{\AA}^2$ , because excitation transfer and Penning ionization (for Xe) become exit channels.

The group of dense Xe ( $6p', 7p, 6d$ ) states in the 10.9-11.1 eV range have been studied in He, Ne and Ar [10,11]. Nearly all of the interstate relaxation cross sections are larger than  $30 \text{\AA}^2$ , even for He and Ne. One conclusion is that no restriction exists for transfer among the  $6p', 7p, 6p$  types of level and, in particular, a change in Xe<sup>+</sup> core from  $^2P_{3/2}$  to  $^2P_{1/2}$  does not limit interconversion of  $6p'$  and  $7p$  states. Another observation was the extremely large cross sections ( $\sim 150 \text{\AA}^2$ ) for several pairs of levels with very small energy defects ( $\sim 30 \text{ cm}^{-1} = 0.004 \text{ eV}$ ) in collisions with He, and perhaps Ne. A Demkov model in which the parallel entrance and exit

channels were coupled over a wide range of internuclear separation explained these very large cross sections [11]. The lowest energy level of this group of levels, Xe(7p[1/2]<sub>1</sub>), has small quenching rate constants in both He and Ne, and relaxation of the Xe\* population from this group of states to the next group (starting with Xe (7s) –10.6 eV) will be by radiative decay for modest pressures of He and Ne as buffer gases.

### 3 Excitation-Transfer Reactions to Atoms

Although it was characterized several years ago, the state specific Ar (4s[3/2]<sub>2</sub>) + Kr reaction can serve as a convenient reference for discussion of excitation-transfer reactions [12,13].



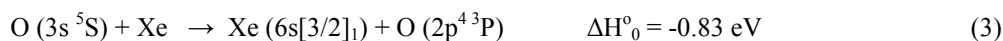
The lower Kr (5p[5/2]<sub>2,3</sub>) states with energy defects of ~0.10 eV are not products for thermal energy collisions. The cross section for formation of Kr (5p[3/2]<sub>2</sub>) increases with velocity over the 500-1500 m s<sup>-1</sup> range with no evidence for a threshold energy [13]. The selectivity for the excitation-transfer process has been explained with a Landau-Zener formulation using Lennard-Jones type entrance and exit channel potentials that were based on scattering data. The repulsive potentials from Kr (5p[3/2]<sub>2</sub>) + Ar and Kr (5p[3/2]<sub>1</sub>) + Ar cross the entrance channel at ~6.0 and ~5.5 Å, respectively. One explanation [12] of the small cross section for Kr (5p[3/2]<sub>1</sub>) formation was that the probability of crossing from the Ar (4s[3/2]<sub>2</sub>) + Kr potential to Ar + Kr (5p[3/2]<sub>1</sub>) was quite small and rate limiting, i.e., nearly diabatic behavior was followed. In this model, the discrimination against the Kr (5p[3/2]<sub>1</sub>) state arises from the much steeper gradient of the exit channel potential at the crossing point. This explanation, however, is not compatible with the positive dependence of the cross section on velocity [13]. An interaction matrix element of 0.03 eV between the entrance and exit channel potentials provided an approximate fit to the velocity dependence of the cross section and to the thermal rate constant for formation of Kr (5p[3/2]<sub>2</sub>). In this formulation, the small cross section arises from the nearly adiabatic behavior at the crossing point. The discrimination against Kr (5p[3/2]<sub>1</sub>) arises because most incoming trajectories follow the Kr (5p[3/2]<sub>2</sub>) + Ar potential. This discussion [13] did not include the Ω substate potentials, because they were not known. However, interstate relaxation from Kr (5p[3/2]<sub>2</sub>) to Kr (5p[3/2]<sub>1</sub>) and from Kr (5p[3/2]<sub>1</sub>) to Kr (5p[5/2]<sub>2 and 3</sub>) does occur in collisions with Ar with rate constants of 1.4 × 10<sup>-11</sup> and 6.7 × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively [12]. Thus, a network of intersecting potential energy curves arising from the Ω substates must exist, and a completely successful model must treat all of the interacting Ω-substate potentials. The quenching rate constant for Ar (4s[1/2]<sub>0</sub>) atoms by Kr is 50 times smaller [14] than reaction (1), because the entrance channel has 0<sup>-</sup> symmetry, whereas the closest exit potential has 0<sup>+</sup> symmetry, because the energy defects for other Kr (5p) exit channels are large, i.e., the crossing positions are unfavorable, and because the interaction matrix elements must be smaller than for Ar (4s[3/2]<sub>2</sub>) + Kr potential(s). Based on reaction (1), cross sections of 1-2 Å<sup>2</sup> per exit channel for cases with weakly interacting, repulsive potentials can be expected. The excitation-transfer cross-sections for the Ar (4s[3/2]<sub>2</sub>) + Xe [15] and the Ar (4p) + Kr [3] reactions increase to 40 and ~30 Å<sup>2</sup>, respectively, mainly as a consequence of the large number of available exit channels plus somewhat larger positions for crossings of the potentials. In contrast, the number of channels is sparse for the Kr (5s[3/2]<sub>2,1</sub>) and Kr (5s[1/2]<sub>0,1</sub>) + Xe reactions [9,16] and those cross sections are 46, 8.2, 69 and 1.1 Å<sup>2</sup>, in order of increasing energy of the Kr\* states; the two large cross sections require especially favorable interaction matrix elements at the crossing points of the potentials to reach ~50 Å<sup>2</sup>.

The quenching of Ar (4s[3/2]<sub>2</sub>) atoms by H atoms and by O atoms can be used to illustrate reactions with very attractive entrance channels that open specific exit channels with large energy defects [15,17].



The O (3p<sup>3</sup>P) atoms can be collisionally relaxed to O (3p<sup>5</sup>P), ΔE = 0.25 eV, in collisions with Ar [15], but the quintet state is not formed directly in reaction (2). The quenching cross sections for H and O atom reactions at room temperature were about 9 and 5 Å<sup>2</sup>, respectively. Quantitative description of the entrance and exit channel potentials is complicated because of the mixing of the zero-order ion-pair and bonding-covalent potentials. Reaction (3) with a thermal cross section of 44 Å<sup>2</sup> [19], presumably involves similar attractive potentials as

reaction (2).



The O(3s<sup>5</sup>S) state is not quenched by Ar because neither excitation transfer or interstate relaxation is possible [20]. Although more examples are needed, it seems that the cross sections per exit channel state for this category of reaction are as large or larger than those for repulsive entrance channel potentials.

As a conclusion for this section, we suggest that excitation-transfer cross sections can scale up to ~ 50 Å<sup>2</sup> if the collider provides a large number of acceptor states. In a few cases the coupling probability between entrance and exit channel potentials may fortuitously be of the magnitude to match the thermal velocity range, and a large cross section can result even for a small number of product states. It should be remembered that the excitation-transfer cross sections will be small if the matrix element becomes so large that the collision pair follows adiabatic behavior.

## 4 Quenching Reactions by Molecules

### 4.1 Excitation-Transfer Reactions to N<sub>2</sub> and CO

The thermal average cross sections for several states of Xe, Kr and Ar reacting with N<sub>2</sub> and CO are listed in Table 2. The cross sections are 1-5 Å<sup>2</sup> for N<sub>2</sub> and 2-10 Å<sup>2</sup> for CO for the lowest energy state of Xe, Kr and Ar. However, the rate constants vary considerably for other states in the (n + 1)s manifold. The cross sections increase to ~ 50 Å<sup>2</sup> for states with 1.5-2.0 eV of additional excitation energy. Quenching of excited states of Xe, Kr and Ar by N<sub>2</sub> and CO proceeds by excitation transfer to give a bound electronically excited N<sub>2</sub><sup>\*</sup> or CO<sup>\*</sup> state with a narrow vibrational distribution and even considerable specificity for the rotational distribution. . Because the CO<sup>\*</sup> and N<sub>2</sub><sup>\*</sup> states fluoresce, these reactions have been studied in great detail and an extensive body of literature exists [27-30]. Frequently, the most favored vibrational level is slightly endoergic, which identifies the entrance channel as a repulsive potential [30]. No one model can explain all details of the product state distributions; however, a transfer between repulsive entrance and exit channel potentials similar to reaction (1), but with the added consideration of coupling to the internal states of N<sub>2</sub> and CO, seems necessary. The reactions of Kr(5s or 5s') atoms with N<sub>2</sub>, but not CO, have unusually small and variable cross sections. This is puzzling, since the Xe(6p) states with similar energy have much larger cross sections. Experiments [31] also have been done to compare the Kr(5p) + N<sub>2</sub> reactions with the Ar(4s[3/2]<sub>2</sub>) + N<sub>2</sub> reaction, which have nearly the same energy. The Kr(5p) states have rate constants of 10-20 × 10<sup>-11</sup> cm<sup>3</sup> s<sup>-1</sup>, and the cross sections are larger than for Ar(4s,4s') atoms. Thus, the nature of the excited atom does matter even though the energy of the entrance channel is quite similar.

The reactions of many of the atomic states in Table 2 have been studied with H<sub>2</sub>. The cross sections increase from 1-5 Å<sup>2</sup> for the (n+1)s states and up to 30-40 Å<sup>2</sup> for Ar(4p) and Xe(6p) atoms. The quenching reaction results in dissociation of H<sub>2</sub>, regardless of whether the mechanism is reactive quenching or excitation transfer to the dissociative H<sub>2</sub>(b<sup>3</sup>Σ<sub>u</sub><sup>+</sup>) state. Based upon recent interpretations [3], at least the Ar(4s and 4p) reactions involve reactive quenching giving ArH<sup>\*</sup> + H, and an analogy exists with the reactions of excited states of alkali metal atom with H<sub>2</sub> [32,33].

Table 2. Quenching rate constants and cross sections for N<sub>2</sub>, CO, CH<sub>4</sub>, Cl<sub>2</sub> and CCl<sub>4</sub>

Atomic State	Energy eV	Rate Constants <sup>a</sup> (Cross Sections <sup>a</sup> )				
		N <sub>2</sub>	CO	CH <sub>4</sub>	Cl <sub>2</sub>	CCl <sub>4</sub>
Xe(6s[3/2] <sub>2</sub> ) <sup>b</sup>	8.32	1.9 (3.6)	3.6 (7.0)	32 (49)	72 (191)	63 (211)
Xe(6s[3/2] <sub>1</sub> )	8.44	1.9 (3.1)	6.3 (12)	33 (49)	69 (186)	78 (262)
Xe(6s[1/2] <sub>1</sub> )	9.57	37 (71)	33 (63)	100 (150)	80 (216)	81 (272)
Xe(6p[3/2] <sub>2</sub> )	9.82	19 (36)	36 (70)		145 (242)	78 (262)
Xe(5d[3/2] <sub>1</sub> )	10.40	7.8 (15)	20 (32)	100 (150)	110 (297)	130 (436)

Xe (7p[5/2] <sub>2</sub> )	10.95		99 (189)	300 (450)	370 (997)	380 (1275)
Kr (5s[3/2] <sub>2</sub> ) <sup>b</sup>	9.92	0.41 (0.70)	5.7 (11)	32 (47)	70 (173)	69 (202)
Kr (5s[3/2] <sub>1</sub> )	10.03	1.4 (2.6)	4.9 (8.8)	75 (110)		68 (199)
Kr (5s'[1/2] <sub>0</sub> )	10.52	0.07 (0.12)	3.9 (7.1)	49 (71)	54 (133)	40 (117) <sup>c</sup>
Ar (4s[3/2] <sub>2</sub> ) <sup>b</sup>	11.55	3.6 (5.8)	1.4 (2.3)	49 (67)	73 (146)	54 (121)
Ar (4s[3/2] <sub>1</sub> )	11.59	0.8 (1.9)	5.2 (11.9)	45 (62)		
Ar (4s'[1/2] <sub>0</sub> )	11.73	1.6 (2.5)	13 (21)	53 (72)	72 (138)	73 (163)
Ar (4p[5/2] <sub>2</sub> )	13.09	35 (56)	50 (80)	74 (98)	140 (280)	
Ar (4p[1/2] <sub>0</sub> )	13.27	14 (23)	27 (43)	60 (80)	170 (340)	
Ar (4p'[1/2] <sub>0</sub> )	13.48	3.2 (5.1)	11 (18)	93 (124)	140 (280)	

- a. Rate constants for 300 K conditions in units of  $10^{-11} \text{ cm}^3 \text{ s}^{-1}$  and cross sections in  $\text{\AA}^2$  [14,20-26].
- b. The lowest energy excited states for Ar, Kr and Xe. These states frequently are labeled as the  $4s \ ^3P_2$ ,  $5s \ ^3P_2$  and  $6s \ ^3P_2$  states in the literature.
- c. This value may be too small; direct comparison of Kr (5s[3/2]<sub>2</sub>) and Kr (5s'[1/2]<sub>0</sub>) gave a ratio of 1.1 for the rate constants.

## 4.2 Polyatomic Molecules and Diatomic Halogen Molecules

Tabulations [20,34] of quenching rate constants exist for the first metastable state,  $(n+1)s[3/2]_2$ , of Ar, Kr and Xe and comparisons recently [16,23] have been made with the rate constant of the first resonance state,  $(n+1)s[3/2]_1$ . More limited studies have been done for the reactions of Xe (6p) and Ar (4p) atoms [3,24]. A set of representative quenching rate constants are shown in Table 2 for CH<sub>4</sub>, Cl<sub>2</sub> and CCl<sub>4</sub>. The mechanism for CH<sub>4</sub> is excitation transfer to dissociative states, that for Cl<sub>2</sub> is reactive quenching giving ArCl<sup>\*</sup>, KrCl<sup>\*</sup>, and XeCl<sup>\*</sup> and that for CCl<sub>4</sub> is a mixture of reactive quenching and excitation transfer.

With the exception of CF<sub>4</sub>, CH<sub>3</sub>H and a few other perfluorinated molecules, which do not have acceptor energy states below  $\sim 10$  eV, most polyatomic molecules quench even the first excited state of Xe with large rate constants that approach the gas kinetic limit [20,34]. The large quenching cross section for Ar (4s[3/2]<sub>2</sub>) + Xe reaction provides a useful analogy for quenching by molecules. The Xe atom has a large number of acceptor states in the 11.5 eV range, and the sum of all the product channels gave the large cross section. For molecules the mechanism is excitation transfer to numerous dissociative molecular states; this mechanism may be aided by attractive entrance channel potentials that sometimes can lead to reactive quenching, as represented by Cl<sub>2</sub> and CCl<sub>4</sub>. Since the total quenching cross sections for the  $(n+1)s$  states already are quite large, the increase in cross section for the  $(n+1)p$  states of Ar and Xe is modest, and typically a factor of two. One change in the mechanism for the higher energy atomic states is the enhancement of the reactive quenching channel because of the crossing of the entrance channel with the ion-pair potential at longer range; examples are XeCl<sup>\*</sup> formation from reaction of Xe (6p) atoms with CCl<sub>4</sub> or HCl [23,24].

The large quenching cross section and the velocity dependence of the cross sections [35,36] suggests that the magnitudes are determined by the long-range interactions of the entrance channel potential. This expectation has been confirmed [34] by the correlation of the magnitude of the cross sections with the  $C_6$  coefficient of the long-range entrance channel potential,  $V(R) = -C_6/R^6$ , for a large number of reagent molecules. The  $C_6$  coefficient is determined by the polarizability and the dipole moment of the reagent molecule. A similar correlation also can be demonstrated between the magnitude of the cross sections and the well depth,  $\epsilon_{LJ}$ , for the Lennard-Jones potential of the reagent molecule and the Ar<sup>\*</sup>, Kr<sup>\*</sup>, or Xe<sup>\*</sup> atom. The latter correlation has become a favored test to identify long-range interactions for quenching of excited-state molecules that have large cross sections.

A simple conceptual model for quenching by polyatomic molecules is that of an absorbing sphere with the radius fixed by the long-range potential, but with exit channels determined by the couplings to the competing molecular acceptor states within the sphere. For most reagents, these couplings, are sufficiently strong to ensure quenching

with a high probability for trajectories that enter the sphere, even though we lack knowledge about how to identify and the acceptor states and the final product distributions. Within this general framework, a few specific points can be made.

- i. Quenching corresponds to energy transfer to the molecule and not to interstate relaxation for the excited atom.
- ii. The excited molecule may dissociate with rupture of more than one bond.
- iii. Within a given manifold of atomic states, the quenching cross sections are similar, i.e. there is no obvious dependence on  $J$ . For example, the cross sections for  $(n+1)s[3/2]_1$  resonance states of Xe and Kr are about 30% larger, on average, than for the  $J=2$  metastable states [16].
- iv. For a given molecule, the rate constants tend to increase with increasing electronic energy of the rare gas atom, e.g., Xe (6p) vs. Xe (6s) or Ar (4p) vs. Ar (4s). This is a consequence of a higher density of acceptor states in the molecule and a slightly larger size of the excited-state atom.
- v. For atomic states of nearly the same energy but different principal quantum numbers, the atomic state with the smaller principal quantum number, e.g., Xe (5d) vs. Xe (6p) or Xe (6p') vs. Xe (7p), tend to have smaller rate constants for the reagent.
- vi. For one-electron transfer processes, such as reactive quenching via the ion-pair potentials, a propensity exists to conserve the ion-core state in the  $\text{Ar}^*$  and  $\text{Kr}^*$ , but not  $\text{Xe}^*$ , reactions [25,26].

## 5 Summary

The energy range of the excited-state rare gas atoms is relatively high, 8.3-13 eV, and this may restrict the transferability of some of the results to other chemical systems. Nevertheless, the dual possibilities provided by the excited outer electron and the unfilled ion-core for attractive interactions in the entrance channel should be a general feature for quenching reactions of excited atoms of non-metallic elements. All three categories of reaction, interstate atomic relaxation, excitation transfer to atoms and to diatomic molecules, and dissociative excitation transfer and/or reactive quenching by polyatomic molecules show evidence for the role of these attractive interactions, which vary in strength depending on the collider. The magnitudes of the rate constants for interstate atomic relaxation and excitation transfer to atoms with a limited number of acceptor states depend in a very sensitive way upon the coupling of entrance to exit channel potentials, and rate constants can have a range of magnitude. However, most polyatomic molecules have a sufficiently high density of energy acceptor states that the quenching rate constants are always large. Although the data base for other non-metallic excited atoms is not so large as for rare gas atoms, the quenching of  $\text{O}(2p^3 3p^5 P)$  [18],  $\text{Br}(4p^4 5s^4 P_{5/2})$  [37] and  $\text{B}(4p^2 P)$  [38] atoms seem to show the same general trends.

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## Appendix

Quenching rate constants for six electronically excited ( $v'=0$ ) molecules<sup>a</sup>

Reagent	PF(A <sup>3</sup> A) <sup>b</sup> 3.6 eV 4.2 $\Phi$ s	CF(A <sup>2</sup> E <sup>+</sup> ) <sup>c</sup> 5.3 eV 26 ns	SiF(C <sup>2</sup> ) <sup>d</sup> 4.9 eV 0.11 $\Phi$ s	SiCl(BN <sup>2</sup> ) <sup>d</sup> 4.4 eV 1 $\Phi$ s	NH(c <sup>1</sup> A) <sup>e</sup> 5.4 eV 0.46 $\Phi$ s	CO(B <sup>1</sup> E <sup>+</sup> ) <sup>f</sup> 10.8 eV 22 ns
He	< 0.002	< 0.4	Small	4.1	$\leq 6 \times 10^{-4}$	0.34
Ar	< 0.006	< 0.4	0.50	7.4	$\leq 6 \times 10^{-4}$	17
CF <sub>4</sub>	< 0.07	< 0.4		> 18		
SF <sub>6</sub>	< 0.07				0.022	
H <sub>2</sub>	40	2.4	75	26	15	21
N <sub>2</sub>	15	6.9	40	7.5	1.3	17
CO	17	21			34	
O <sub>2</sub>	36	16			20	59
CO <sub>2</sub>	9.0		14	18	21	81
CH <sub>4</sub>	16	4.0	9	18	25	65
NH <sub>3</sub>	98				81	
H <sub>2</sub> O					79	131

a. The units are  $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for 300 K conditions.

b. J. Xu, D.W. Setser and R. Hamman, *J. Phys. Chem.*, **99** (1995) 3173. The quenching constants for the PF(d<sup>1</sup>A) state (4.4 eV) are, on average, two times larger than for the PF(A<sup>3</sup>A) state. The isoelectronic SO(A<sup>3</sup>A) state also has large quenching rate constants.

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d. S. Singleton and K.C. McKendrick, *J. Phys. Chem.*, **97** (1993) 1389; C. W. Watson and M.G. McKendrick, *Chem. Phys.* **96** (1994) 79; N.A. Jackson, C.J. Randall and K.C. McKendrick, *J. Phys. Chem. A*, **102** (1998) 51. Since a large fraction of the quenching for both SiF(C) and SiCl(BN) corresponds to conversion to the B<sup>2</sup>E<sup>+</sup> states, state-to-state data are available; K. G. McKendrick, *J. Chem. Soc. Faraday Transactions*, **94** (1998) 1921.

e. R.D. Kenner, F. Roher and F. Stuhl, *J. Phys. Chem.*, **93** (1989) 7824. These authors point out that the quenching cross sections for NH (c<sup>1</sup>A) are nearly identical to those for OH (A<sup>2</sup>E<sup>+</sup>) for a common reagent. The rate constants for NH(A<sup>3</sup>A) are, on average, one half as large as those for NH (c<sup>1</sup>A). The database for quenching of OH (A<sup>2</sup>E<sup>+</sup>) is very large.

f. F.D. Teodoro, J.E. Rehm, R.L. Farrow and P.H. Paul, *J. Chem. Phys.*, **113** (2000) 3046. Quenching occurs by collisional transfer to CO (b<sup>3</sup>E<sup>+</sup>) and by excitation transfer for some of the molecular colliders.