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COLLISIONAL QUENCHING OF $K^*(4p^2P)$ AND $K^*(5p^2P)$ BY H_2O, CF_4, AND CH_4

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Although a number of workers have studied the gas-phase collisional quenching of the lowest excited configuration of the alkali atoms,[1] very little is known about the quenching of higher energy configurations. In contrast to Hg and rare gas atoms which have also been the subjects of many studies, the excitation energies of the alkali atoms are typically less than the bond energies of molecules which are efficient quenching agents. For example, the excitation energies (in e.V.) of the first six excited configurations of K are: 1.61 ($4p^2P$), 2.60 ($5s^2S$), 2.67 ($3d^2D$), 3.06 ($5p^2P$), 3.40 ($4d^2D$), and 3.41 ($6s^2S$). Nevertheless, a variety of molecules are quite efficient at quenching the lowest excited configuration of the alkali metals, although certain "saturated" molecules, such as CH_4, CF_4, and, to a lesser extent, H_2O are inefficient as quenching agents.[1,2] The work described here was undertaken in order to determine whether this inefficiency would persist for higher energy configurations. Measured rate constants are presented for quenching of $K^*(4p^2P)$ and $K^*(5p^2P)$ by H_2O, CF_4, and CH_4.

The apparatus and experimental procedure was similar to that described in Ref. 2. All measurements were made with ultraviolet radiation from a hydrogen arc which passed through a monochromator with a triangular bandpass function, 60Å FWHM, and impinged upon a quartz cell containing KI vapor at 890°K. The $K^*(4p^2P)$ fluorescence intensities at 7665Å

and at 7699Å, which were produced by photodissociation of the KI at 2450Å, were isolated by different interference filters. Irradiation at 1925Å permitted measurement of the $K^*(5p^2P)$ fluorescence through an interference filter which transmitted both the 4044 and 4047Å resonance lines. With the UV intensity held constant at one of these two wavelengths, the rate constant, k_q, for quenching of the corresponding 4p or 5p potassium fluorescence was determined by admitting a known number density, n, of quenching gas to the KI cell and fitting the measured fluorescence intensity, R_n, to the Stern-Volmer relation:

$$R_0/R_n = 1 + \tau k_q n. \qquad (1)$$

The radiative fluorescence lifetimes, τ, were assigned values[3,4] of 2.6×10^{-8} sec. for $K^*(4p^2P)$ and 1.4×10^{-7} sec. for $K^*(5p^2P)$. Thus, k_q is determined by assuming that the resonance fluorescence is produced by the direct photodissociation of KI to give the corresponding $K^*(4p^2P)$ or $K^*(5p^2P)$ configuration. This clearly holds for production of $K^*(4p^2P)$ at 2450Å because threshold for production of $K^*(5s^2S)$ by photodissociation of KI in its ground vibrational level is calculated[5] to be 2060Å. Calculated thresholds for production of $K^*(5p^2P)$ and $K^*(4d^2D)$ (or K^* $(6s^2S)$) are at 1920 and 1820Å respectively. The measured reduced $K^*(5p^2P)$ fluorescence efficiency (i.e., the ratio of fluorescence intensity to incident UV intensity) peaks at ∿ 1900Å and decreases to 20% of its peak value at ∿ 1760 and 2020Å, indicating that very little of the $K^*(5p^2P)$

fluorescence produced by 1925Å can be due to initial production of higher energy configurations. This was further verified in an auxiliary experiment in which no variation was observed in k_q for CH_4 quenching of the $K^*(5p^2P)$ fluorescence produced by irradiation of KI at 1925, 1950, and 1975Å.

Measured values of k_q are listed in Table I. Measurements at 7665Å and 7699Å determined the same k_q value for $K^*(4p^2P)$ + H_2O. For $K^*(4p^2P)$ + CH_4 or CF_4, where k_q was too small to measure reliably, some collisional mixing of the two fine structure levels was observed. In contrast to work in Ref. 2 where the translational energy dependence of k_q was measured, k_q values listed in Table I were determined for thermal distributions. Relatively large pressures of quenching gas ($\sim$ 20 torr for H_2O, $\sim$ 50 torr for CF_4 and CH_4) were necessary to determine the slow quenching rates of $K^*(4p^2P)$, so that the initial $K^*(4p^2P)$ speed distribution should have collisionally relaxed before being quenched. In experiments on $K^*(5p^2P)$ + CH_4 and CF_4, a few torr of the quenching gas was pre-mixed with $\sim$ 650 torr of Ar, and this mixture (at a reduced pressure) was admitted to the KI cell in order to insure that the $K^*(5p^2P)$ speed distribution was thermalized by collisions with Ar. In separate experiments, it was ascertained that pure Ar (at $\sim$ 600 torr) or pure Xe (at $\sim$ 200 torr) failed to produce a measurable attenuation of the $K^*(5p^2P)$ fluorescence intensity. This "Ar thermalizing" procedure was not used in measuring k_q for $K^*(5p^2P)$ + H_2O due to experimental difficulties. Here,

however, the distribution in relative collision speeds is primarily determined by the thermal speed distribution[2] of H_2O by virtue of its light mass relative to K. This was verified with $K^*(5p^2P) + CH_4$ where a value of $6.7 \pm 0.7 \times 10^{-10}$ cm^3/sec was measured for k_q in the absence of the "Ar thermalizing" procedure, in reasonable agreement with the thermal value given in Table I.

We are not aware of any previous studies on the quenching of K resonance fluorescence by CH_4 or CF_4. Flame fluorescence studies of $K^*(4p^2P) + H_2O$ have determined quenching cross sections of $2.8 \pm 0.9 Å^2$ at 1400 - 1800°K[6] and $2.6 \pm 0.3 Å^2$ at ∿ 2000°K,[7] in reasonable agreement with our result in view of the temperature differences. On the other hand, the only previous study[7] of $K^*(5p^2P)$ determined (at 2000°K) a quenching cross section for H_2O of $10 \pm 4 Å^2$, substantially different from the result obtained here.

In Ref. 2, we chose to compare our measured cross sections, Q_q, for quenching of $Na^*(3p^2P)$ with cross sections, Q_D, for "close encounters" wherein the incident trajectories surmount the centrifugal barriers in the effective potentials associated with the long-range attractive dispersion forces. In doing so, we did not propose that Q_q should equal Q_D because (1) the description of the quenching collision must include some matrix element coupling different electronic states and (2) Q_D provides only an estimate of the cross section for close encounters because of neglect of shorter range forces.

Nevertheless, this comparison proved useful in assessing the efficiency of different molecules for quenching $Na^*(3p^2P)$. Molecules with appreciable electron affinities (e.g., I_2 and SO_2) are "super-efficient" with $Q_q > Q_D$, unsaturated molecules (e.g., N_2 and C_2H_4) as well as some potentially reactive compounds (e.g., CF_3Cl) are efficient quenchers with $Q_q \lesssim Q_D$, and certain saturated molecules (e.g., H_2O, CF_4 and CH_4) are very inefficient with $Q_q << Q_D$. A similar comparison, shown in Table I in the form of rate constants (k_q/k_D) rather than cross sections, indicates that H_2O, CF_4, and CH_4 are also very inefficient at quenching $K^*(4p^2P)$. For $K^*(5p^2P)$, however, H_2O, CH_4, and, to a lesser extent, CF_4 prove to be quite efficient as quenching agents.

The quenching collisions studied here refer to some unknown combination of inelastic processes producing lower K configurations and reactive processes. For H_2O and CF_4, especially, the large efficiency for quenching of $K^*(5p^2P)$ might simply be a consequence of the relatively large reaction exoergicities listed in Table I; this point of view is advanced by Dowling, et. al.[8] in discussing their results on quenching of $Na^*(3p^2P)$ and $Tl^*(7s^2S)$. At any rate, the failure of Ar or Xe to quench $K^*(5p^2P)$ suggests that H_2O, CF_4, and CH_4 quench this configuration either by reaction or by an inelastic process wherein electronic energy is at least partially converted into vibrational and rotational excitation. Furthermore, the failure of CH_4 to efficiently quench

$Hg^*(6p^3P_{0,1})$,[9] despite the larger excitation energies, suggests that the dramatic difference shown in Table I is not simply a consequence of higher density of vibrational - rotational levels in the quenching molecules corresponding to the higher $K^*(5p^2P)$ excitation energy.

One possible mechanism for the efficient quenching of $K^*(5p^2P)$ would picture the collision as proceeding via a charge-transfer intermediate which could produce lower K configurations or an "ionically bound" KX product. This venerable model of collisional quenching of excited alkali atoms has recently been employed to interpret[10] the quenching of $Na^*(3p^2P)$ by N_2; it may also be operative[11] in the related (not precisely inverse) process of electronic excitation in collisions of fast alkali atoms. Appearance potentials of 5.0 - 5.7, $\sim$ 7.5, and 4.7 eV have been reported for dissociative electron attachment to H_2O,[12] CH_4,[12] and CF_4,[13] respectively, whereas vertical electron affinities of $\sim$ -3 to $\sim$ -4 eV would appear to be necessary in order to account for the observed contrasting efficiencies for quenching of $K^*(4p^2P)$ and $K^*(5p^2P)$ in terms of this charge-transfer model. However, these dissociative electron attachment results may not refer to excitation of the lowest negative ion resonance states. Indeed, Claydon, et. al.[14] have reviewed the known data on negative ion states of H_2O and have concluded that the lowest resonance state is not seen in dissociative electron attachment because it is bound relative to dissociation into OH^- + H,

suggesting a vertical electron affinity greater than -3.28 eV, probably between -2 and -3 eV. In terms of the simple charge transfer model, a value near -3 eV would seem to account for the large value of k_q for $K^*(5p^2P)$, the relatively small values of k_q for $K^*(4p^2P)$ and $Na^*(3p^2P)$, as well as the trend[1] of increasing k_q on proceeding from $K^*(4p^2P)$ to $Rb^*(5p^2P)$ and $Cs^*(6p^2P)$. Similarly, Christophorou and Stockdale[15] have suggested that the lowest energy dissociative electron attachment observed in CH_4 proceeds via excitation of a core-excited resonance level. Thus, it seems plausible to attribute the quenching behavior of H_2O, CH_4, and CF_4 observed here to formation of charge-transfer intermediates involving the lowest energy resonance states of the negative ions. It should also be noted, however, that the increasing density of electronic terms with increasing excitation energy might be expected to lead to avoided crossings and efficient quenching even in the absence of formation of such a charge-transfer intermediate.

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Table I. Measured quenching rate constants, k_q, at 890°K.

K configuration	quenching gas	$10^9 k_q$ $(cm^3/sec)^a$	Q_q $(Å^2)^b$	$k_q/k_D{}^c$	ΔD_o $(eV)^d$
$4p^2P$	CF_4	<0.01	<1	<0.01	1.3(KF + CF_3)
$4p^2P$	CH_4	<0.01	<1	<0.01	-0.9(KH + CH_3)
$4p^2P$	H_2O	0.024±0.008	1.5	0.025	0.0(KOH + H)
$5p^2P$	CF_4	0.21±0.04	26	0.16	2.8(KF + CF_3)
$5p^2P$	CH_4	0.77±0.08	60	0.45	0.6(KH + CH_3)
$5p^2P$	H_2O	1.0±0.1	85	0.71	1.5(KOH + H)

[a]The uncertainty given for each k_q value is simply the standard deviation provided by a least squares fit of the pressure dependence of the fluorescence intensity to Eq. (1). The true error in k_q should be somewhat larger.

[b]Quenching cross section, calculated as $k_q = Q_q < g >$, where $< g >$ is the thermal average relative speed.

[c]As discussed in the text, k_q/k_D is a measure of the quenching efficiency.

[d]ΔD_o is the exoergicity of the possible reaction; data from Ref. 5.

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