

ELECTRONIC EXCITATION OF K ATOMS
IN COLLISIONS WITH DIATOMIC MOLECULES:
THRESHOLDS AND ENERGY DEPENDENCE FROM 1-5 eV

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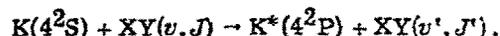
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A velocity selected atomic potassium beam produced by sputtering has been utilized to study collisional excitation of K atoms by diatomic molecules. $K^*(4^2P)$ was detected by its radiative decay. For N_2 , NO and O_2 the excitation thresholds coincide with the endoergicity of the $4^2S \rightarrow 4^2P$ transition, 1.6 eV (c.m.s.) whereas for CO the threshold occurs at 2.1 eV. The cross sections rise about linearly with velocity above threshold and are of the order of 2\AA^2 at 4 eV.

There is not much accurate information about translational-to-electronic energy transfer, and one finds some belief that at least for small molecules this process must be inefficient. A little more is known about the process of quenching of resonance radiation, and genuine lifetime measurements for the first excited state of alkali atoms in the presence of perturbing gases have recently given precise values for some quenching cross sections [1-6]. These experiments show that the quenching cross sections are very small ($< 10\text{-}2\text{\AA}^2$) for collisions with inert gases, but large ($30\text{-}50\text{\AA}^2$) for collisions with H_2 and N_2 . This difference has customarily been attributed to electronic-to-vibrational energy transfer, although for diatomic molecules there is no evidence that resonance with vibrational levels has much influence on the quenching cross section [1, 5, 7]. Recently developed spectroscopic [7] and electron impact [8] techniques now permit analysis of the vibrational excitation deposited in the quenching molecules. For three systems studied thus far [7], the vibrational excitation accounts for roughly 1/3 to 2/3 of the electronic quantum, and almost all the rest must go into translation. Some quantitative evidence for

efficient vibrational-to-electronic energy transfer has also been obtained, primarily by observing fluorescence of Na^* resulting from collisions with N_2 or CO molecules vibrationally excited in a shock wave [9], microwave discharge [10], or hot furnace [11].

The present work deals with collisional transition of K atoms to the first excited electronic state by impact with diatomic molecules,



Were it not for concurrent vibrational and rotational transitions ($v, J \rightarrow v', J'$), this would be the inverse of quenching. As it is, possible differences between these processes may shed some light on the vibrational effects. Similar beam studies of collisional excitation of K by rare gases, small molecules, and hydrocarbons have been performed at Harvard [12, 13]. A fast K atom beam (1-60 eV, lab) produced by charge-exchange of an ion beam was used. With such a beam it is difficult to get quantitative data at the low end of the energy range, although for N_2 and several other molecules the results [13] indicate that the thresholds for excitation are at, or not much higher than, the endoergicity for the $4^2S \rightarrow 4^2P$ transition, 1.61 eV (c.m.s.). Particularly for comparison with quenching studies, it is desirable to determine accurately the cross sections in the threshold region. In the 1-10 eV range, sputtering seems to be the best method of producing an atomic beam. We report in this

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letter our first measurements of collisional excitation of K by N_2 , NO, CO, O_2 . In each case the reaction threshold has clearly been found.

The apparatus employs a sputtering atomic beam source similar to that of ref. [14], but pulsed for velocity selection like that in refs. [15] and [16]. The energy resolution has been compromised to be $\Delta E/E = 0.20 \times (E[\text{eV}])^{1/2}$, where ΔE is the full width at half maximum. The beam is detected by surface ionization.

After velocity selection the beam passes through a scattering chamber containing the target gas at 10^{-3} torr pressure. The $\lambda = 7680 \text{ \AA}$ resonance line is filtered out by a Schott type R 62 filter on the blue side and the multiplier efficiency curve at the red side. So far, the signal to noise ratio has only partially been maximized.

The results are shown in fig. 1. The abscissa scale is linear in relative velocity (proportional to $E^{1/2}$). The absolute ordinate scale is not very well known; an estimate good within a factor of 3 at both sides is 100 units $\approx 1 \text{ \AA}$. The relative

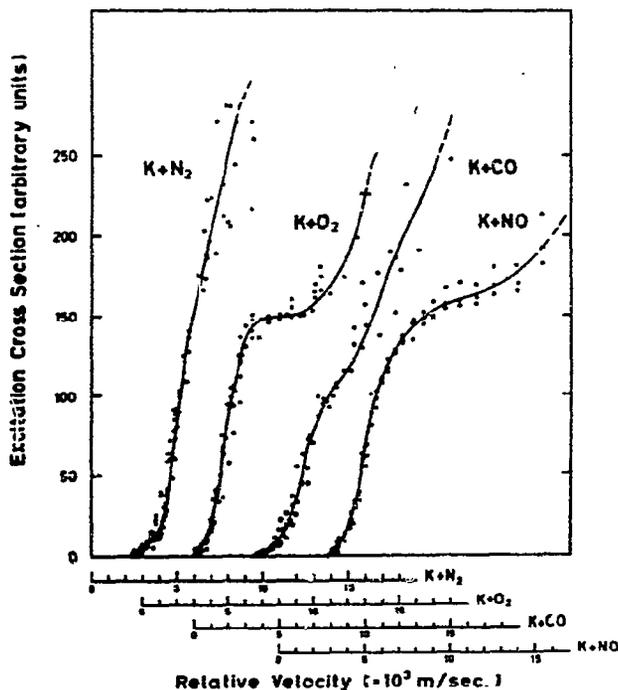


Fig. 1. Excitation cross sections for K colliding with the molecules indicated. The abscissas have been shifted for clarity. At a velocity of 10 km/sec the c.m.s. energies are 8.5, 8.5, 8.8 and 9.1 eV for N_2 , CO, NO and O_2 respectively.

ordinates are as good as the calibration factors of our ionization gauge for different gases, i.e. $\approx 20\%$. The total cross sections at 1-2 eV above threshold are of the order of $\approx 1 \text{ \AA}^2$, somewhat less but not in contradiction to the results of ref. [12].

In all cases, the excitation functions rise linearly, the tail at threshold being due to the limited energy resolution. One can show that after linear extrapolation of the linear part a resolution dependent shift gives the correct thresholds. Within the experimental uncertainty of about ± 0.2 eV, for N_2 , NO, and O_2 the excitation thresholds coincide with the endoergicity, 1.6 eV, whereas for CO the threshold is definitely higher, about 2.1 eV. Since the resolution is rather low and deteriorates as the energy is increased, our data are incapable of revealing much structure in the cross section, and one should consult refs. [13] and [12] for the shape of the cross section above ≈ 4 eV (c.m.s.) energy (≈ 7 km/sec velocity).

As the target gases were at room temperature, the initial vibrational state is the ground state. Thus in these experiments $v = 0 \rightarrow$ some range of v' (and the most probable $J \approx 7$ or 8 \rightarrow some range of J'). Our results for N_2 , NO, O_2 imply that at threshold the final vibrational state is $v' = 0$, or, considering the experimental uncertainty, at most $v' = 1$ (the vibrational quanta are 0.2-0.3 eV). For CO, the higher threshold we find could be due to negligible probability for electronic excitation without concurrent vibrational excitation (postulate $v = 0 \rightarrow v' \approx 2$ to account for the 0.5 eV increment). However, participation of the $v = 0 \rightarrow v' = 0$ or 1 channels cannot be ruled out, since the higher threshold might arise instead from a bona fide activation energy (e.g., postulate a curve-crossing located above 1.6 eV).

In thermal energy quenching experiments $v' = 0 \rightarrow$ some range of v (and most probable $J' \approx 7$ or 8 \rightarrow some range of J). For a specified $v, J \rightarrow v', J'$ path, microscopic reversibility relates the excitation cross section to that for the corresponding quenching process by

$$\sigma_e/\sigma_q = [g'/g] [(2J'+1)/(2J+1)] [1 - (\Delta/E)],$$

where $\Delta(v, J; v', J')$ is the endoergicity. The electronic degeneracy factor $g'/g = 3$ if all multiplet components of $K^*(4^2P_{3/2}, 2^2P_{1/2})$ participate equally; otherwise g'/g is closer to unity. The CO case is of particular interest, as the 0.5 eV increment found in the threshold for σ_e and the large size of σ_q at thermal energies imply that the $v' = 0 \rightarrow v = 0$ channel must be negligible

compared with $v > 0$ channels in the quenching process. This information complements the results found for $\text{Na}^+ + \text{CO}$ in the infrared emission experiments [7], which cannot detect $v = 0$ molecules. The emission spectrum indicates that the quenching rate is negligibly small for $v > 4$ and becomes large for the lower states, although as yet the shape of the distribution over $v = 1, 2, 3$ has not been resolved. For the other systems, we can roughly estimate the $v' = 0 \rightarrow v = 0$ component of the quenching cross section. We assume it has no significant energy dependence (over the small range relevant to thermal conditions), in agreement with the experimental temperature dependence and theoretical calculations [17, 18] and assume $J' = J$ for both quenching and collisional excitation. The reversibility relation then requires

$$\sigma_Q(00) = [d\sigma_e(00)/dE][\Delta, 3],$$

where the slope $d\sigma_e/dE$ is evaluated at the excitation threshold and 00 denotes the $v' = 0 \rightarrow v = 0$ channel. Our experimental estimates of the slope must be very crude but yield $\sigma_Q(00) \approx 0.2$ to 1 \AA^2 , values smaller than the observed total quenching cross sections by an order of magnitude or more. Thus, again the conclusion is that most of the quenching proceeds into excited vibrational (and rotational) states.

The prevailing qualitative picture for reactions involving interchange of electronic, translational, and vibrational energies is that these are "locally nonadiabatic" processes, in which the colliding system "jumps" from one potential energy surface to the other only in the vicinity of surface crossings or avoided crossings. All theoretical discussions indicate that the large alkali quenching cross sections must be a consequence of crossings governed by ionic configurations such as $\text{K}^+(\text{XY})^-$. Recently, the first calculations capable of predicting the actual distributions of energy converted to vibration and translation in $\text{Na}^+ + \text{XY}$ quenching have been reported [17, 18]. These calculations employ electron impact data, Franck-Condon factors for comparable iso-electronic systems, and semi-empirical correlations to guess the potential crossing parameters and transition matrix elements. The same procedure can be used to calculate the cross sections for collisional excitation. In agreement with the presently available experimental information, both treatments indicate that resonance effects are insignificant, and something like half or less of the energy goes into vibration. Some adjustment of potential parameters evidently will be required to accommodate our threshold results,

since these calculations yield $\sigma_Q(00) \ll 0.1 \text{ \AA}^2$ for N_2 . Also, elastic scattering data for $\text{Li} + \text{N}_2$, CO , NO , O_2 [19] indicate the repulsive wall for Na or K occurs at appreciably larger distances than estimated in ref. [18]. According to the model used, this must be offset by increasing the value guessed for the polarizability of the N_2^- ion from 10 \AA^3 to something like 60 \AA^3 , in order to enable the K^+N_2^- configuration to provide a crossing compatible with the observed 1.6 eV threshold. It happens that such an increase in $\alpha(\text{N}_2^-)$ will also increase $\sigma_Q(00)$ to about $1 - 2 \text{ \AA}^2$, as shown in auxiliary calculations cited in ref. [18]. This preliminary comparison appears promising and illustrates how data such as ours, together with that from the vibrational analysis experiments [7, 8], can now be used to determine the most sensitive parameters in the semi-empirical theory as well as to test forthcoming electronic structure calculations [20] for crossing potential surfaces.

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