VELOCITY DEPENDENCE OF EXCITATION TRANSFER FROM Ar($4\,^3P_2$) TO Kr

Mattanjah S. DE VRIES, Vojislav I. SRDANOV, George W. TYNDALL and Richard M. MARTIN
Department of Chemistry, University of California, Santa Barbara, CA 93106, USA

Received 10 September 1984; in final form 29 November 1984

The cross section velocity dependence for the excitation transfer process $Ar(4\,^3P_2) + Kr \rightarrow Ar + Kr(5p[3/2]_2)$ was studied using a crossed molecular beam time-of-flight method. The cross section increases with increasing velocity, with no apparent threshold down to 500 m/s. A curve crossing model is found to agree qualitatively with the results, and explains the state selectivity of the quenching process.

1. Introduction

Electronic excitation transfer (ET) between atoms and molecules plays a role in a variety of physical and chemical processes, such as those in plasmas, gas lasers, and in astrophysics. In order to clarify the mechanisms of ET a number of experiments have been reported involving metastable rare gases. Examples are the flowing afterglow experiments of Piper et al. [1] and beam experiments by Winicur et al. [2] on ET from metastable argon atoms (Ar*) to Kr. We have previously studied the velocity dependence of the ET cross section for Ar^*/N_2 [3], and of the ET branching ratios for Ar^*/Cl_2, Br_2 and Kr^*/Cl_2, Br_2 [4]. With the halogen systems a double curve crossing is thought to be responsible for ET, involving the ion pair intermediate.

The case of Ar*/Kr is a special one, not only because the target is an atom, but also because the quenching of $Ar(^3P_{0,2})$ by Kr appears to be state selective, i.e. $Ar(^3P_2)$ is quenched while $Ar(^3P_0)$ is not [1,2] This observation has been used by Golde and Poletti [5] to obtain state selected $Ar(^3P_0)$ in flowing afterglow experiments. Piper et al. [1] have measured the spectrum of the Kr* fluorescence from Ar*/Kr collisions. They find that 90% of the Kr* emission is from the $5p[3/2]_2$ level, and the rest is from the $5p[3/2]_1$ level. Most of the light is emitted at 760.2 nm, which is from the transition of the $5p[3/2]_2$ level to the metastable $^3P_2$ state. The evidence shows that essentially all the quenching of Ar* by Kr is due to ET to these two Kr states, i.e. the total quenching rate is essentially the same as the chemiluminescence rate. Winicur et al. [2] measured the differential scattering of Ar* by Kr and found evidence for the formation of metastable $Kr(^3P_{2,0})$ in the quenching process. They concluded from their results that the metastable Kr* is formed with very little recoil energy. Consideration of the energetics shows that this requires the metastable Kr* to be formed by a two step process:

$$Ar(^3P_2) + Kr \rightarrow Ar + Kr([3/2]_{1,2}), \quad (1a)$$

$$Kr([3/2]_{1,2}) \rightarrow Kr(^3P_{2,0}) + h\nu . \quad (1b)$$

Therefore the entire ET process can be monitored by observing the $Kr([3/2]_{1,2})$ chemiluminescence.

In the present work we report on a study of the velocity dependence of the Ar* to Kr excitation transfer cross section. The results are explained by a direct curve crossing mechanism (i.e. not involving an ionic intermediate state), which also explains the state selectivity of the quenching process.

2. Experimental

The time-of-flight (TOF) apparatus for the study of chemiluminescent cross section velocity dependence has been described elsewhere [3]. A metastable Ar* beam was velocity dispersed by TOF and crossed with an effusive Kr target beam. The effusive Ar beam from

a source operated at 400 K passed through a Penning ionization discharge to form metastable Ar^* [6]. High Rydberg states and ions are not expected to escape from the Penning discharge source, but as a precaution sweeper plates were placed downstream to remove them from the beam. The Ar^* beam was pulsed by a rotating wheel and intersected the Kr beam after a 29 cm flight path. The effusive Kr source was operated at 140 K and was chopped with a beam flag in order to substract background radiation. Metastables were observed by detecting electrons ejected from a Ta target. The chemiluminescence from $Kr(5p[3/2]_2)$ at 760.2 nm was isolated by an interference filter centered at 760 nm with a 10 nm bandwidth, and detected by a red-sensitive photomultiplier tube (RCA C31034). Both metastables and photons were counted as a function of flight time, using a multichannel interface to a minicomputer. From these data we obtain the velocity dependence of the chemiluminescence cross section.

3. Results and discussion

The ET cross section as a function of collision velocity is given in fig. 1. The cross section rises with velocity, but the excitation curve shows no indication of an energy barrier down to 30 meV, i.e. any barrier must be much less than this energy. Winicur et al. [2] concluded from combining their molecular beam inelastic scattering results with flowing afterglow rate constants that the ET cross section rises steeply from a threshold energy of about 25 meV, and they used the threshold model $\sigma(E) = \sigma_0(1 - E_0/E)^n$ to fit their data. This model is incompatible with the present results, since it gives a negative second derivative ($d^2\sigma/dE^2$) whereas our data show a positive second derivative. Winicur et al. also suggested that threshold energies are a general feature of ET cross sections. This does not appear to be true in the present case, nor is it expected if the cross section is controlled by a curve crossing mechanism in the attractive region of the incoming potential.

The relevant potential curves are given in fig. 2, adapted from ref [1]. The $Ar^* + Kr$ curves are obtained from scattering experiments [2,7]. The $Ar + Kr^*$ curves are deduced by comparison with Ar + Rb potentials, also obtained from elastic scattering experiments [8] The coupling between the $Ar^* + Kr$

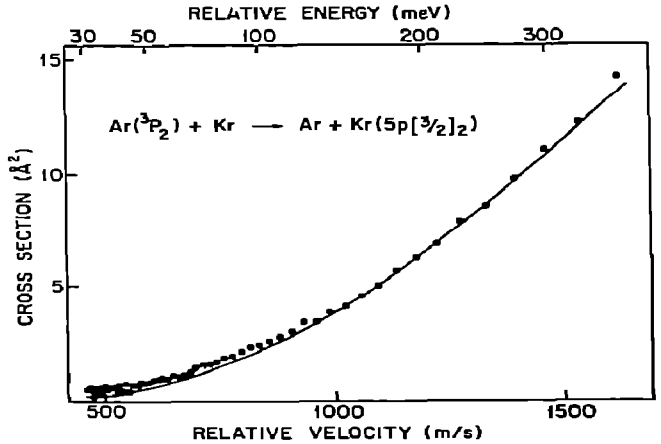

Fig 1 Cross section as a function of relative velocity for reaction (1a). Points are experimental and the solid line is calculated as described in text.

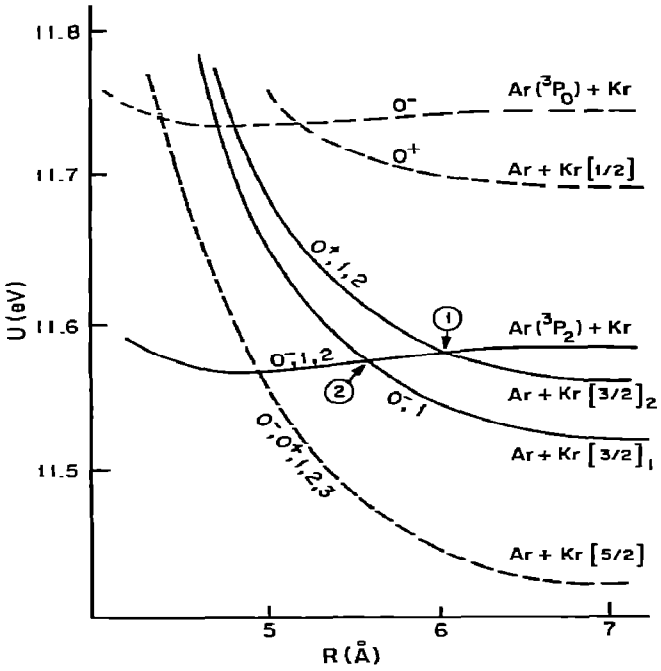

Fig. 2. Schematic Ar–Kr potential curves relevant to the experiment The three potentials that are believed to be of prime importance in the quenching of $Ar(^3P_2)$ by Kr are indicated by solid lines. The two important curve crossings are marked 1 and 2, as discussed in the text.

potentials and the $Kr^* + Ar$ potentials either takes place over a long range of internuclear distances, due to the small separation of some of the levels, or it is a localized curve crossing. The latter possibility can be tested very well by measuring the velocity dependence of the cross section. By isolating the 760 nm radiation in our experiment we have singled out the coupling with the $Ar + Kr(5p[3/2]_2)$ potential, which is the main channel.

According to Landau–Zener theory the probability for staying on the same diabatic potential at a curve crossing is given by:

$$p = \exp(-2\pi H_{12}^2/h v_r \Delta V) \quad (2)$$

H_{12} is the coupling matrix element between the two potentials; ΔV is the difference in potential gradients, and v_r is the radial velocity, all evaluated at the crossing distance R_c. The probability for transferring from one diabatic potential to another is $1 - p$. The crossing point is passed twice, once on the incoming trajectory and once on the outgoing trajectory. For ET to occur the system has to transfer to another diabatic potential on one of those occasions and not on the other, so if there is only one crossing the ET probability is given by $p(1 - p)$. According to fig. 2 there are in fact several crossings. Therefore the model should be refined by allowing all the pathways that can lead to ET. We will only consider the crossings indicated in fig 2 as 1 and 2, since they lead to the only two important product channels. The Landau–Zener probabilities will be p_1 and p_2 respectively. The probability of producing $Kr(5p[3/2]_2)$ is given by:

$$P = (1-p_1)p_1 + p_1(1-p_1)(1-p_2)^2 + p_1 p_2^2(1-p_1). \quad (3)$$

For a given relative velocity v, the radial velocity v_r depends on the impact parameter b. To obtain the cross section for formation of $Kr(5p[3/2]_2)$ as a function of relative velocity, we integrate eq (3) over all reactive impact parameters,

$$\sigma(v) = 2\pi \int_0^{R_c} P(v, b)\, b\, \mathrm{d}b\,. \quad (4)$$

This equation assumes straight-line trajectories up to $R_c(1)$ and $R_c(2)$, which is a valid approximation given the magnitude of the relative velocity and the long range of the crossing distances.

The experimental $\sigma(v)$ data of fig. 1 were fitted with eqs. (2)–(4), using H_{12} as a variable parameter and assuming for simplicity that it is the same at both crossings. The solid line in fig 1 was calculated with $H_{12} = 30$ meV. The close agreement may be somewhat fortuitous, since there are several inaccurately known parameters in the calculation. However, we conclude that the general trend is described very well by the model. The magnitude of the calculated cross section curve is determined mainly by the values for $H_{12}^2/\Delta V$ and $R_c \approx 6$ Å, obtained from the potentials.

The rate constant can be calculated with the equation

$$k = \int_0^\infty f(v)\, v\, \sigma(v)\, \mathrm{d}v\,, \quad (5)$$

where $f(v)$ is the Maxwell–Boltzmann velocity distribution. For a temperature of 300 K, we obtain rate constants of 2×10^{-12} cm^3 s^{-1} for producing $Kr(5p[3/2]_2)$ and 3×10^{-14} cm^3 s^{-1} for producing $Kr(5p[3/2]_1)$. This may be compared with the experimental values of 5.6×10^{-12} and 0.65×10^{-12} cm^3 s^{-1} respectively, determined by Piper et al. [1]. The lack of quantitative agreement between our model and the experimental rate constants is not surprising, considering the approximations in the model. Fitting the model to our excitation function for $Kr(5p[3/2]_2)$ formation gives a rate constant which is about 1/3 of the experimental value, but the calculated rate constant for $Kr(5p[3/2]_1)$ formation is much further from the experimental value. This may be mainly due to our assumption that H_{12} is the same at both crossings, which does not affect the shape of the $Kr(5p[3/2]_2)$ excitation function as strongly as it affects the $[3/2]_1/[3/2]_2$ ratio ‡.

It is not surprising that $Ar(^3P_{0,2})$ is not quenched to produce Kr([5/2]), since the probability $p_1 p_2$ to survive the first two crossings is very small. In considering the various possible curve crossings it is noted that the symmetries of the states have to be the same for radial coupling to be effective. The relevant symmetries are indicated in fig. 2. It is assumed that splitting

‡ Professor Krenos and coworkers [9] have recently measured the [3/2] excitation function in a beam–gas experiment to collision energies greater than 1 eV, and find that the function reaches a maximum at about 1 eV, whereas our calculated curve would have a maximum at about 8 eV. This also indicates the need for improvement of the model.

between states of different symmetry, that are degenerate at large separation, becomes important only at internuclear distances much smaller than the ones relevant here. It is immediately clear that $Ar(^3P_0) + Kr$ cannot couple with all the exit channel states. Furthermore the curve crossing probability depends upon the factor $H_{12}^2/\Delta V$ While H_{12} is not known for these crossings, the differences in ΔV alone are not sufficient to explain the state selectivity of the $Ar(^3P_{0,2})$ quenching. In order to explain the fact that the rate constants for quenching of $Ar(^3P_0)$ to Kr(5p[3/2]) states is much smaller than for quenching of $Ar(^3P_2)$, it is necessary to assume that H_{12} for the $Ar(^3P_0)$ crossings is either at least an order of magnitude larger or an order of magnitude smaller than for the $Ar(^3P_2)$ crossings.

We conclude that the velocity dependence of this atom–atom excitation transfer is very different from the previously studied atom–molecule cases [3,4]. The mechanism does not seem to involve an ionic intermediate, and we did not observe a threshold. Our results can be explained by a neutral curve crossing mechanism. In order to explain the state selectivity of the Ar*/Kr quenching we must assume a very different coupling matrix element for the crossings involving the $Ar(^3P_0)$ state. It is possible that the stronger coupling of the $Ar(^3P_2)$ + Kr state with the Ar + Kr([3/2]) product states is the result of their near resonance.

Acknowledgement

Financial support for this work was provided by the US Department of Energy, Office of Basic Energy Sciences (Grant DE-AM03-76SF00034)

References

[1] L.G. Piper, D.W. Setser and M.A.A. Clyne, J. Chem. Phys. 63 (1975) 5018.
[2] D.H. Winicur, J.L Fraites and J. Bentley, J. Chem. Phys. 64 (1976) 1724
[3] T.P. Parr and R.M. Martin, J Chem. Phys. 69 (1978) 1613.
[4] M.S de Vries and R.M. Martin, Chem. Phys. 80 (1983) 157.
[5] M.F. Golde and R.A. Poletti, Chem. Phys. Letters 80 (1981) 18
[6] F. Bozso, J.T Yates Jr., J. Arias, H. Metiu and R M Martin, J. Chem. Phys. 78 (1983) 4256.
[7] T. Nenner, Entropie 42 (1971) 142.
[8] E.V. Nikifarov and L E. Scherba, Opt. Spectry 32 (1972) 567.
[9] J. Krenos, private communication