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Quenching of metastable Ar, Kr, and Xe atoms by oxygencontaining compounds: A resonance fluorescence study of reaction products

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Quenching of electronically excited Ar, Kr, and $Xe({}^{3}P_{0,2})$ atoms by diatomic and triatomic oxygen-containing compounds has been studied by atomic resonance fluorescence in a discharge-flow system at room temperature. Absolute branching ratios for molecular fragmentation in the quenching reactions have been obtained, showing that this channel is dominant in many cases. While single R–O bond cleavage is usually the favored process, cleavage of both bonds of H₂O occurs in nearly 50% of quenching collisions with Ar^{*}, and evidence is obtained for analogous atomization of NO₂ and SO₂ by Ar^{*}. Emission by electronically excited fragment species has been found to be mostly weak; thus, dissociative excitation is a minor channel except for the reactions of Ar^{*} with N₂O and H₂O.

I. INTRODUCTION

In recent years, the rate constants for quenching of metastable electronically excited noble gas atoms (A*), $He(2^{1,3}S)$, and Ne to $Xe [np^5(n+1)s^3P_{0,2}]$ by a wide range of simple molecules have been measured, ¹⁻⁶ yielding values close to the collision rate in most cases. Many studies of product channels have also been made. For He* and Ne*, chemi-ionization has been found to be the dominant channel, ⁵⁻⁹ although the data for Ne* as yet are sparse. For Ar*, Kr*, and Xe*, light emission from energy transfer

$$A^* + BC - A + BC^* , \qquad (1)$$

$$- \mathbf{A} + \mathbf{B}^* + \mathbf{C} , \qquad (2)$$

or from noble-gas halide excimer formation

$$A^* + RX \rightarrow AX^* + R \tag{3}$$

has been observed from many reactions¹⁰⁻¹⁵ and detailed studies made in a few instances. For instance, anomalous rotational distributions in the N₂($C^{3}\Pi_{u}$) state, formed from reaction of Ar* with N₂, were observed several years ago¹⁶ and shown, recently, ¹⁷ to differ significantly in the reactions of Ar(³P₂) and Ar(³P₀). Novel emission channels, such as

$$Ar^* + COCl_2 - Ar + CO + Cl_2^* (Ref. 18), \qquad (4)$$

$$Ar^* + SCl_2 \rightarrow Ar + S + Cl_2^* (Ref. 10)$$
(5)

have also been observed.

However, these studies provided no information on the branching ratios for these emission channels (1)-(5)and thus no overall understanding of the A* quenching mechanisms was possible. Very recently, ^{19,20} it has been concluded that channel (3) is dominant for reaction with halogen molecules (secondary predissociation of ArCl, ArBr, ArI, and KrI leads to intense atomic halogen emission^{21,22}), but for the other quenching agents, with a few notable exceptions, the excimer emission represents a minor channel. Similarly, channels (1) and (2) are rarely dominant (reactions of Ar* with Kr²³ and N₂O²⁴ have been found to be exceptions). For several quenching agents, Penning ionization by Ar* is exothermic and ions have been detected, ^{14,25} but no branching ratios were measured.

The present study is part of a project to determine the major products of quenching of the metastable states of Ar, Kr, and Xe, which have excitation energies, respectively, of 11.55, 9.92, and 8.32 eV for the ${}^{3}P_{2}$ states and 11.72, 10.56, and 9.45 eV for the ${}^{3}P_{0}$ states. This project is of direct relevance to excimer lasers and other discharge and plasma systems. More generally, it is hoped that such data can be applied to reactions of other excited species, extending the realm of relevance to fields such as flames and atmospheric chemistry. The specific question addressed in this paper is the importance of "dark channels," those in which no ionization or emission is observed. It is expected that dissociation of the reagent is the most likely such channel and this is being studied by atomic resonance fluorescence of the products. Of major interest is the relative importance of simple bond cleavage releasing an atom, e.g.,

$$Ar^* + H_2O - Ar + H + OH$$
 (6)

and molecular elimination [cf. Eqs. (4) and (5)], such as

$$Ar^* + H_2O \rightarrow Ar + O + H_2 . \tag{7}$$

The results for several oxygen-containing compounds are presented in this paper and molecular dissociation found, indeed, to be the major channel for most of these reagents.

II. EXPERIMENTAL

A single discharge-flow system, illustrated in Fig. 1, has been used for both emission and resonance fluorescence studies of the reactions of metastable Ar, Kr, and Xe atoms. Ar, or mixtures of Kr or Xe in Ar, were excited in a weak dc discharge 300 V, 1 mA between cylindrical tantalum electrodes, and flowed into a 7 cm diameter Pyrex observation vessel, mounted in the entrance port of a vacuum monochromator (Minuteman 305 MV, half-meter Czerny-Turner). Because of the high linear velocity of the gas, typically 50 ms⁻¹ in

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FIG. 1. Experimental reaction vessel. A: movable reagent loop; B, C: reagent inlets; W: MgF_2 window; M: microwave cavity.

the 1 cm diameter inlet tube, the flow emerges as a jet, which retains its shape throughout the observation region. Reagents were usually added through the concentric inlet tube sometimes with a small flow of Ar carrier gas, and reacted on diffusing into the jet of metastable atoms, producing a conical reaction flame, visible for some reagents. The movable reagent loop injector A, shown in Fig. 1, was not used in most experiments reported here.

The whole inlet assembly was made movable through the use of an O-ring seal to the observation vessel. For emission studies, the assembly was fully raised, bringing the reaction flame fully into the field of view of the monochromator. For resonance fluorescence, the assembly was lowered; the reaction flame occurred largely out of the monochromator field of view, while the reaction products flowed upwards, where they were illuminated by radiation from a resonance lamp. The lamp employs flowing gases, excited by a microwave discharge. In the current design, shown in Fig. 1, used for detection of H and O atoms, the Pyrex lamp is attached to the observation vessel by means of an O-ring seal, which also supports a cylindrical Teflon light baffle, to which a MgF_2 window is attached by epoxy cement. With this design, the microwave cavity can be placed within 1 cm of the window and, even at discharge powers as low as 10 W, the plasma extends to the window. In early experiments, atomic oxygen lines were generated by flowing O_2 and He through the lamp. Later, the O_2 was replaced by H_2O_1 , held in a trap at 0 °C and swept into the lamp by a small flow of He. Typically, the total He flow rate through the lamp was 200 μ mol s⁻¹

at a pressure of 2 Torr, and the H_2O concentration was 5×10^{12} to 2×10^{13} cm⁻³. The $O({}^3S - {}^3P_J)$ line intensity ratio was about 2:2:1, compared to 5:3:1 for a completely unreversed source. This He/H₂O mixture proved to be a stable, reproducible, bright source of both O and H lines, at 130 and 122 nm, respectively (as well as of OH emission), and was used for the experiments presented here.

Emission and resonance fluorescence from the reactions were dispersed by the vacuum monochromator and detected by one of three photomultipliers. For vacuum UV emission (λ <190 nm) and for the resonance fluorescence studies, a solar-blind photomultiplier (EMR 542G) was used in the pulse-counting mode. Near UV emission was detected by an EMI 9789QB, and visible and near IR emission (300-900 nm) by a cooled RCA C31034-02 phototube (with this detector, the 2400 g/mmholographic diffraction grating was replaced by a 1200 lines/mm ruled grating). For the last two detectors, the output was measured directly on a picoammeter, the dark currents being typically 0.2 and 0.06 nA, respectively. In all cases, the output could be obtained on strip chart recorders. The spectral responses of the detectors were measured by recording vibrational progressions of band systems of N_2 , CO, H_2 , and NO, and, for the region 400-900 nm, the air afterglow from the reaction of O atoms with NO.26

Although the data presented in this paper are basically relative emission or fluorescence intensities, provision was made for absolute measurements. Absolute concentrations of atoms for calibration of the resonance fluorescence system were prepared by titration reactions using inlets B and C (Fig. 1). For instance, Br atoms were prepared quantitatively by adding small measured flows of Br_2 to an excess of discharged O_2

$$O + Br_2 - OBr + Br$$
, (8)

$$O + OBr \rightarrow O_2 + Br$$
, (9)

and O atoms by the reaction

$$N + NO - N_2 + O . \tag{10}$$

Concentrations of the metastable argon atoms were determined by IR absorption measurements. An Oriel spectral calibration lamp was mounted opposite to the entrance slit of the monochromator and IR lines [811.5 nm for $Ar({}^{3}P_{2})$ and 794.8 nm for $Ar({}^{3}P_{0})$] detected by the RCA photomultiplier. For these experiments, the dc discharge was modulated at 1 or 10 Hz and the signal processed by an Ortec 9315/9320 pulse counting system, operated in the synchronous counting (chop) mode. Previous measurements²⁷ with a similar lamp have found an effective emission Doppler temperature of about 3700 K; this value was used in analyzing the measured absorption by Ar* atoms.

Flow conditions were chosen to maximize signals. For reactions of Ar*, the typical Ar flow rate and pressure were 300 μ mol s⁻¹ and 1.2 Torr. The resulting measured concentration of Ar(³P₂) was $1-2\times10^{10}$ cm⁻³, with that of Ar(³P₀) a factor of 5-10 smaller. For study of Kr* and Xe*, the Ar carrier flow rate and pressure were typically 600 μ mol s⁻¹ and 3.0 Torr. Under these conditions, the Ar* and Xe* concentrations were similar and approximately one-half that of Ar* at the lower pressure, while the Kr* concentration was typically a further factor of 2 smaller. A range of concentration was used for each reagent molecule, typically 2×10^{13} to 4×10^{14} cm⁻³.

The carrier gases Ar (Matheson UHP) and He (Matheson HP) were purified further by passage through a redhot copper furnace and a dry-ice-cooled silica-gel trap at atmospheric pressure, followed by a liquid-N2 cooled trap at low pressure. The Kr was Matheson, Research Purity, and the Xe, Matheson CP grade (99.9% minimum). Of the reagent gases, NO was passed through Ascarite and purified further by bulb-to-bulb distillation, and OCS was pumped on at 77 K, these gases being stored in bulbs; O_2 , CO_2 , CO_2 , N_2O_2 , and SO_2 were used directly from lecture bottles. For all these gases, flow rates were measured by the capillary pressure drop method. H₂O (deionized) was stored in a cold trap at low pressure and swept into the reaction vessel by a small Ar flow. NO_2 was stored in a cooled trap in a section of line separated from the reaction vessel by a needle valve. The NO₂ partial pressure in this line (0.1 to 1 Torr) was monitored by absorption of Xe resonance lines at about 470 nm and the vapor swept into the reaction vessel by Ar carrier gas, whose flow rate (about 10 μ mol s⁻¹) and pressure (about 100 Torr) were also measured. This procedure allowed determination of the NO₂ flow rate.

III. RESULTS

A. Resonance fluorescence studies

Absorption measurements of the $Ar(^{3}P_{2})$ metastables revealed concentrations of $(1-2) \times 10^{10}$ cm⁻³, and lower concentrations of Kr* and Xe* metastables were expected. At these concentrations of atoms such as O, H, and Br, and a path length of 1 cm, as used in this system, the resonance fluorescence intensity is expected to be accurately proportional to atom concentration, irrespective of the resonance lamp line shape.²⁸ No detailed tests were carried out with the present lamp configuration, but the expectation was confirmed for Bratom resonance fluorescence in earlier experiments, in which Br atoms were generated by Reactions (8) and (9) and a collimated-hole-structure was used to collimate the lamp output. From the data acquired for Br-atom concentrations in the range 3×10^{10} to 3×10^{11} cm⁻³, it was confirmed that the resonance fluorescence signal varies linearly with [Br] up to about 10^{11} cm⁻³.

Because of the low atom concentrations, monochromator slit-widths of 1 mm were used, equivalent to a resolution of 0.7 nm. This prevented separation of the $O({}^{3}P_{J})$ spin-orbit states; under the conditions used, the oxygen atoms suffer more than 1000 collisions while in the detection region, and a Boltzmann distribution among the states is expected. Because of the resulting modest fluorescence intensities, great care was taken to allow for background contributions to the measured signals. The major background was scattered light from the lamp, which was measured with the dc discharge source of the metastable atoms switched off. Back-



FIG. 2. The dependence of emission intensities at 130 nm on $[O_2]$ in the reaction of Ar* with O_2 . • Background emission, measured with only the dc discharge on; o scattered light, from the resonance lamp; I the resonance fluorescence signal.

ground emission from the Ar^{*}₂ continuum and from the Ar^{*} + Q reaction was also measured and both background signals were subtracted from the total signal with both discharges on, to yield the resonance fluorescence signal. With the most recent lamp configuration, typical signals in the reaction of Ar^{*} with O₂ were: a scattered light level of 10 count s⁻¹, a background emission signal of less than 2 s⁻¹ and a resonance fluorescence signal of $100-150 \text{ s}^{-1}$. The resonance fluorescence signals from Kr^{*} and Xe^{*} + O₂ were smaller, but usually greater than 50 s^{-1} . The absolute O-atom calibration showed that these signals represented O-atom concentrations of typically $(1-5) \times 10^{10}$ atom cm⁻³.

The dependences of scattered light, background emission, and resonance fluorescence intensity on reagent concentration for $Ar^* + O_2$ are shown in Fig. 2. Once sufficient O_2 has been added to quench all the metastable atoms, further addition has no effect on the background emission or the scattered light from the lamp; further, the resonance fluorescence signal varies little with $[O_2]$. the small increase probably not being significant. These results help confirm the validity of the technique. Firstly, absorption of the 130 nm radiation by O_2 does not cause a significant depletion of the signal, in accord with known absorption coefficients.²⁹ Next, the O atoms detected clearly do not arise from photodissociation of the O_2 . Thirdly, there is no evidence of depletion of the O atoms by secondary reactions, again as expected. The resonance fluorescence signal thus represents the O-atom concentration following complete reaction of the Ar* with O_2 . Comparison of the signal with that obtained by interaction of Ar* with another reagent allows determination of the relative yields of O atoms in the two reactions. In subsequent tests, the reference reaction with O₂ was always included to allow for any drifts in Ar* concentration or lamp output. A similar

TABLE I. Ar*+NO: Dependence of O-atom resonance fluorescence intensity on NO concentration.

10 ⁻¹³ [NO] cm ⁻³	Resonance fluorescence intensity (Hz)		
2.0	110.5±2%		
4.3	122.5		
7.1	137.1		
10	141.0		
15	136.2		

routine was adopted for the reactions of Kr* and Xe*.

Results similar to those in Fig. 2 were found for the reactions of Ar*, Kr*, and Xe* with CO₂, CO, OCS, SO₂ (except for Kr* + SO₂ at very high SO₂ concentrations—see Sec. IV), and for H₂O (no flow rates were measured for this reagent but the temperature of the cooled reservoir was varied over a wide range). N₂O absorbs very strongly at 130.1 nm, resulting both in a 20% decrease in the scattered light intensity at the highest concentration used $(2 \times 10^{14} \text{ cm}^{-3})$ and in the absence of a true plateau in the resonance fluorescence signal. The data were corrected for the absorption using published absorption coefficients³⁰; these predict absorptions roughly 80% of that of the scattered light, which presumably does not follow the most direct path through the reaction vessel.

For the reaction of Ar* with NO, as shown by the data in Table I, the resonance fluorescence signal rose with reagent concentration much more rapidly than in the reaction with O_2 . This is due to the secondary reaction

$$N + NO - N_2 + O , \qquad (11)$$

which has a rate constant³¹ of between 2×10^{-11} and 6×10^{-11} cm³ s⁻¹, depending on the electronic state of N. The observed variation could not be modeled be-



FIG. 3. The dependence of the measured O-atom resonance fluorescence signal $I(NO_2)$ from the reaction $Ar^* + NO_2$ on NO_2 concentration. $I(O_2)$ is the O-atom signal from the reference reaction $Ar^* + O_2$. The various symbols refer to separate experiments.

cause of the complexity of the reagent mixing region, in which the NO concentration is not uniform; instead, most data were obtained at high NO flow rates, with the reaction time maximized by use of low pumping speeds in an attempt to drive Reaction (11) to completion. The results, analyzed on this assumption, lead to a lower limit to the true O-atom yield.

The reactions with NO_2 are more difficult to analyze than those with NO, as a secondary reaction *removes* O atoms

$$O + NO_2 - NO + O_2 , \qquad (12)$$

for which $k = 9.5 \times 10^{-12}$ cm³ s⁻¹. As shown in Fig. 3 for the reaction with Ar*, it was not possible to drive the primary reaction to completion without the secondary reaction occurring. Again, no simple quantitative analysis of the plot was possible and only a lower limit to the true O-atom yield can be estimated from the maximum in the curve.

The oxygen atom yields relative to those from the reactions of Ar*, Kr*, and Xe* with O_2 , which are set arbitrarily equal to 2, are listed in Table II; these are discussed in Sec. IV. The observation of O atoms from the reactions of Ar* and Kr* with H₂O prompted a careful study of O and H production in the reactions with H₂O and D₂O. The H(D) yields were compared to those from the reactions wth H₂(D₂). The results are listed in Table III.

B. Emission studies

The resonance fluorescence results show that molecular dissociation is a major channel for the reagents studied. This channel includes dark channels, in which all fragments are formed in nonemitting states, and dissociative excitation [Eq. (2)], in which the molecular fragment is formed in an emitting excited electronic state. Although emission has been observed previously in many of the reactions studied here, branching fractions are available only for the reactions of Ar* with N₂O and OCS.²⁴ Therefore, emission from the reactions of Ar* with CO₂, SO₂, H₂O, and NO₂ was investigated. For all these

TABLE II. Relative oxygen atom yields.

Reagent	Ar*	Kr*	Xe*	
O ₂	2	2	2	
CO_2	0.98 ± 0.02	1.02 ± 0.08	0.98 ± 0.02	
SO_2	0.94 ± 0.04	0.96 ± 0.06^{a}	1.00 ± 0.02	
N ₂ O	1.12 ± 0.02^{b}	1.04 ± 0.06^{b}	0.82 ± 0.04^{b}	
co	0.84 ± 0.02	0 ± 0.02	0 ± 0.02	
OCS	0.10 ± 0.02	0.12 ± 0.02	0.06 ± 0.02	
NO	$\geq 1.38 \pm 0.06^{\circ}$	$\geq 1.34 \pm 0.04^{\circ}$	$\geq 1.66 \pm 0.04^{\circ}$	
NO ₂	$>0.98\pm0.06^{d}$	•••	•••	

^aAt low [SO₂]. The O-signal decreases to 0.80 ± 0.06 at high [SO₂].

^bCorrected for absorption of 130 nm radiation by N₂O. The raw data are Ar*: 1.02 ± 0.04 ; Kr*: 0.96 ± 0.04 ; Xe*: 0.76 ± 0.04 .

^cLower limits, as the secondary reaction $N + NO \rightarrow N_2 + O$, may not have been driven to completion.

^dLower limit, as removal of O by $O + NO_2 \rightarrow NO + O_2$ is occurring.

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 $D_2 + O$

2D + O

(A) Relative C Results for D)- and H(D)-atom ;) ₂ O in parentheses	yields $[O_2 = 2, H_2(I_2)]$	$D_2) = 2].$
	Ar*	Kr*	Xe*
$O(^{3}P)$ yield	0.46 ± 0.04	0.14 ± 0.04	0 ± 0.02
H viold	(0.48 ± 0.02)	(0.10 ± 0.02)	(0 ± 0.02)
ii yielu	(1.42 ± 0.06)	(1.08 ± 0.08)	(1.00 ± 0.14)
(B)Branching	fractions.		
H+OH	$0.54 \pm \mathbf{0.04^a}$	$0,86 \pm 0.04$	1.00 ± 0.06
$H_2 + O$	0	0.03 ± 0.03	0 ± 0.06
2H + O	$\textbf{0.46} \pm \textbf{0.05}$	0.11 ± 0.05	Endothermic
D + OD	0.52 ± 0.04	0.90 ± 0.02	$1 00 \pm 0 14$

^aThe branching fractions for formation of OH($X^2\Pi$) and OH($A^2\Sigma^+$) are, respectively, 0.26 ± 0.09 and 0.28 ± 0.09.

 0 ± 0.04

 0.10 ± 0.04

 0 ± 0.14

Endothermic

 0.03 ± 0.03

 0.45 ± 0.05

reagents, the strongest emissions occur in the near UV and the integrated intensities were compared with that of $N_2(C^3\Pi_u - B^3\Pi_g)$ from the reaction of Ar* with N₂, for which the branching fraction has been measured as 0.60 \pm 0.09³² and nearly unity³³; a value of 0.80 \pm 0.20 was used in the present work. In each case, the reagent concentration was adjusted to obtain the maximum emission intensity, the flame, under these conditions, lying completely within the field of view of the monochromator (reagent inlet assembly fully raised). The emitting states detected and preliminary branching fractions are listed in Table IV. For SO₂, NO₂, and H₂O, the observed emitting states are sufficiently short-lived for all emission to occur within the field of view of the monochromator. Even the longest-lived states observed $NO(B^2II)$ and $OH(A^2\Sigma^*)$ are expected to suffer negligible quenching^{31,34,35} and the spectra can be compared directly with the $N_2(C-B)$ system. The reaction $Ar^* + CO_2$ yields $CO(a^3\Pi)$, which has a radiative lifetime of about 7 ± 2 ms,³¹ and is thus largely pumped out of the detection volume. Direct estimation of the fraction emitting within the detection volume is hazardous as the reagent mixing zone occupies an appreciable part of the field of view. The emitting fraction was therefore estimated experimentally by observing the quenching of the emission by small additions of H₂, which quenches $CO(a^3\Pi)$ rapidly³¹ $(k=1.8\times10^{-10} \text{ cm}^3 \text{ s}^{-1})$, but quenches Ar* a factor of 9 more slowly than does CO_2 .¹ Data at two concentrations of CO₂ are included in Fig. 4, together with calculated fits. These use a model based on visual inspection of the conical reaction flames, namely formation of $CO(a^{3}II)$ in a step function at the cone, and radiative loss and quenching by H_2 and CO_2 downstream. The CO(a), CO_2 , and H_2 were assumed to be homogeneously distributed within the jet downstream of the cone, and bulk flow of the gas was assumed. The length of the observation region was fixed by the geometry of the optical system but the cone height was allowed to vary. Both quenching of CO(a) by CO_2 and of Ar^* by H_2 were included, the latter being monitored directly by intensity



FIG. 4. Dependence of CO(a-X) emission intensity from Ar* +CO₂ on added H₂. I_0 : no H₂. (i) $[CO_2] = 1.3 \times 10^{14} \text{ cm}^{-3}$: o: experimental points; — calculated with flame cone height = 1.5 cm; (ii) $[CO_2] = 0.73 \times 10^{14} \text{ cm}^{-3}$: I: experimental points; - - - calculated, with cone height = 2.0 cm.

measurements of the $H_2(a^3\Sigma_e^*-b^3\Sigma_u^*)$ continuum. The best fits to the data gave reasonable cone heights which, as expected, decreased as the CO₂ concentration was increased. It was concluded that 4.3% of the CO(*a*) emits within the observation region, with an uncertainty, including that in the radiative lifetime, of about $\pm 50\%$.

The reaction of Ar* with H_2 provides a further instance of emission accompanying a dissociative channel. The characteristic blue flame is due to a continuum, peaking at about 290 nm, ascribed to the $H_2(a-b)$ transition.¹⁰ The lower state is repulsive, dissociating to ground-state H atoms. The intensity of the continuum was measured in order to estimate the fraction of dissociative events, which occur via the $H_2(a)$ state.

TABLE IV. Observed dissociative excitation channels in the reactions of Ar*.

Reagent	Emitting states	Branching fraction
$\overline{CO_2}$	$CO(a^3\Pi), v = 0-2$	0.16±0.08
SO_2	SO($A^{3}\Pi$), $v = 0-6$ SO($B^{3}\Sigma^{-}$)	0.03 ± 0.01
H_2O	OH($A^{2}\Sigma^{+}$), $v = 0, 1$	0.28 ± 0.09
NO ₂	NO($A^2 \Sigma^*$, $B^2 \Pi$, $D^2 \Sigma^*$, $B'^2 \Delta$)	~0.13
H ₂	$H_2(a^{3}\Sigma_{g}^{+})$	0.05

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IV. DISCUSSION

This section has three main aims: (i) to establish that molecular dissociation is a major reaction channel, for the reagents studied; (ii) to introduce an unexpected form of dissociation of the triatomic quenching agents, direct fragmentation into three atoms; and (iii) to discuss the product distributions in terms of models of energy transfer, with particular emphasis on the role of charge transfer in these reactions.

A. Branching fractions for dissociation

The data of Table II show that CO₂, SO₂, and N₂O give O atom yields, which are consistently about onehalf of those given by the reactions of O_2 , suggesting that O₂ is dissociated into two atoms, while the other reagents suffer a single R-O bond cleavage. This conclusion is consistent with a previous study of Ar* + + N₂O, ²⁴ which found N₂($B^{3}\Pi_{g}$) to be the dominant product, and with an EPR study of $Ar^* + O_2$,³⁶ as well as with consideration of other channels in the O_2 reaction. Penning ionization of this molecule is endothermic and no ions are detected in reaction with Ar*.³⁷ Direct excitation transfer to nondissociative states of O_2 is less easy to rule out as many such states are metastable and would emit only weakly. Very weak IR emission was detected from $O_2(b^1\Sigma_{\ell}^*)$ in the reaction of Ar* with O2; however, the strong dependence of the intensity on O_2 concentration implies that it arises via a secondary process

$$O(^{1}D) + O_{2} - O_{2}(b^{1}\Sigma_{\ell}^{*}) + O(^{3}P)$$
 (Ref. 38), (13)

and that $O_2(b^{1}\Sigma_{\ell}^{*})$ is not a major primary product of Ar* + O_2 . As this state has a radiative lifetime of about 12 s,^{39,40} other excited states of O_2 should be detectable in our system if they are produced efficiently. Their absence is thus taken as evidence against nondissociative energy transfer as a major quenching channel.

Reaction (13) raises the important possibility that dissociation of O_2 produces significant quantities of O atoms in states, which are not detected by the present $O({}^{3}P)$ resonance fluorescence technique. Any $O({}^{1}D)$ formed suffers quenching by Ar or O_2 . That by Ar alone is sufficiently rapid⁴¹ for the lifetime of $O({}^{1}D)$ in the present system to be less than 0.1 ms, sufficiently small to ensure that, in the resonance fluorescence experiments, complete deactivation occurs before the gas reaches the observation region. Both Ar and O_2 quench $O({}^{1}D)$ to the ground state, so that $O({}^{1}D)$ atoms are not distinguished from primary $O({}^{3}P)$ atoms [an estimate of the primary yield of $O({}^{1}D)$ in the reaction of Ar* with O_2 is presented elsewhere⁴²].

Formation of $O({}^{1}S)$ is exothermic in the reactions of Ar* and Kr* with O_2 . $O({}^{1}S)$ is quenched slowly by Ar and O_2^{41} and would not be detected by $O({}^{3}P)$ resonance fluorescence. $O({}^{1}S{}^{-1}D)$ emission has been reported¹⁰ from the reaction with Ar* and our studies confirmed the presence of very weak 557.7 nm emission. Formation of $O({}^{1}S)$ was shown to be a very minor channel by studying $O({}^{3}P)$ resonance fluorescence from Ar* + O_2 in the presence of NO, at concentrations sufficient to quench $O({}^{1}S)$ to $O({}^{3}P)$ but insufficient to quench Ar* appreciably. No significant change in the fluorescence signal on addition of NO was seen. This discussion implies that the data in Table II can be interpreted as absolute O-atom yields, and they thus give the branching fractions for those dissociation channels, which lead to release of a single oxygen atom.

Having established that molecular dissociation is the dominant channel for reactions of O₂, CO₂, SO₂, and N₂O, we wish to consider the results for each reagent in more detail. CO₂ appeared to show the simplest behavior in its reactions, closely analogous to that of O_2 . Any $O(^{1}D)$ would be guenched rapidly to $O(^{3}P)^{41}$ and detected. $O(^{1}S)$, which would be quenched only slowly, was shown to be a minor product by comparison of the 557.7 nm line intensities from the reactions of Ar* with CO_2 and O_2 . The small yields of $O(^1S)$ and $CO(a^3\Pi)$ in the reaction with CO₂ agree with a previous, less quantitative study.⁴³ The reaction of Ar* with N₂O gave an atomic O yield which, after correction for absorption of 130 nm radiation by N_2O , was slightly higher than expected. As the other principal product is $N_2(B^3\Pi_{\epsilon})$, which emits to the metastable $N_2(A^3\Sigma_{\mu}^*)$ state, it is possible that the excess O atoms result from a secondary process

$$N_2(A^3\Sigma_u^+) + N_2O - 2N_2 + O$$
. (14)

A small yield of NO + N has been detected in a previous study²⁴ of $Ar^* + N_2O$ and may arise from approach of the Ar^* to the end nitrogen atom of N_2O .

Great care was taken in the reactions with SO_2 , as this reagent quenches $O(^{1}D)$ rapidly and by a chemical reaction⁴¹

$$O(^{1}D) + SO_{2} \rightarrow SO + O_{2} \quad . \tag{15}$$

In the reaction with Ar*, the O-atom signal changed by less than 5% when the SO₂ concentration was varied between 1.1×10^{13} and 5×10^{14} cm⁻³; quenching of O(¹D) by SO₂ is slight at the lower end of the range and dominant at the upper end. It was concluded that O(¹D) is not a significant product of Ar* +SO₂. In the reaction with Kr*, in contrast, the O-atom signal dropped significantly when the SO₂ concentration was increased over a comparable range (see footnote to Table II). This was ascribed to O(¹D) formation in approximately 20% of Kr* +SO₂ quenching collisions and the value entered in Table II is that at low SO₂ concentration.

For CO, dissociation by Kr* and Xe* is endothermic and, even for reaction with Ar*, the yield is significantly below unity. This result is consistent with the observation of emission from several excited states of CO, including $c^{3}\Pi$, $b^{3}\Sigma^{+}$, $a^{3}\Pi$, and $A^{1}\Pi$; the latter state appears to be the strongest emitter.

For NO, only lower limits to the O-atom yields were obtained; however, this includes contributions from $O(^{1}D)$ and $O(^{1}S)$, which are rapidly quenched to $O(^{3}P)$.⁴⁴ The data imply that at least 69% of the reaction with Ar* yields atoms. This result is consistent with information on other possible channels; no appreciable emission from the parent molecule is seen, but saturation ion measurements³⁷ show that approximately 28% of the reaction occurs via chemi-ionization. Ionization is probably a contributing channel also in the reaction of Kr*

with NO.

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Very low yields of O atoms were seen in the reactions of Ar*, Kr*, and Xe* with OCS, although conditions favoring quenching of $O({}^{1}D)$ to $O({}^{3}P)$ were used. Chemi-ionization is exothermic in the reaction with Ar* and has a branching fraction³⁷ of 0.30. Emission spectra show appreciable CO and S-atom emission and it is expected that fragmentation into CO+S, including dark channels, accounts for the residue of the reactions and is the major channel. The low yield of O+CS would thus be analogous to that of N+NO in the reaction with N₂O.

The detection of O atoms from the reactions of Ar^{*} and Kr^{*} with H_2O was surprising. Secondary reactions of H or OH with H_2O or Ar^{*} can be excluded as a source and, indeed, the detected yields were independent of H_2O flow rate over a factor of 5 (estimated from the temperatures of the H_2O reservoir). The resulting O and H atom yields were analyzed in terms of the processes

$$Ar^* + H_2O - Ar + H + OH , \qquad (16)$$

$$-\operatorname{Ar} + \operatorname{H}_{2} + O \qquad (17)$$

$$- Ar + 2H + O . \tag{18}$$

Channel (18) is exothermic by 2.0 eV and the analogous reaction of Kr* by 0.5 eV. The results, listed in Table III, show that channel (17) is of negligible importance, but channel (18) accounts for half of the reactions of Ar* with H_2O and D_2O . It should be noted that $O(^1D)$ formation is endothermic for this channel; any $O(^1D)$ formed by channel (17) would be quenched by Ar to $O(^3P)$ at the lowest H_2O concentrations used and so would not invalidate the analysis.

The results for NO_2 are the least certain, as discussed in Sec. III. The lower limits to the O atom yields again show dissociation to be the dominant channel, assuming that O + NO is the major product. The negligible yields of parent emission and of chemi-ionization³⁷ are consistent with this, as is the detection of strong NO emission. However, two independent experiments suggest that for $Ar^* + NO_2$ the true O yield may be significantly higher and that some atomization

$$Ar^* + NO_2 - Ar + N + O + O \tag{19}$$

is occurring. Firstly, resonance fluorescence intensities from the reactions of Ar* with excess CO_2 or SO_2 are reduced by about 30% when NO_2 , at a concentration of 1×10^{13} cm⁻³, too small to compete for removal of Ar*, is added. This implies that appreciable reaction of O atoms with NO_2 [Reaction (12)] is occurring even at the peak of Fig. 3. Secondly, a preliminary search for N atoms was carried out, using low reagent concentrations $\gtrsim 10^{13}$ cm⁻³. Under these conditions, product atoms such as N and O, at concentrations of $\sim 10^{10}$ cm⁻³, can compete weakly with the parent molecule for reaction with residual Ar*, giving characteristic vacuum UV emission

$$Ar^{*}+O(^{3}P) \rightarrow Ar+O(3^{3}S)$$
, (20)

$$O(3^{3}S) \rightarrow O(^{3}P) + h\nu(130 \text{ nm}) \quad (\text{Ref. 45}) , \qquad (21)$$

$$Ar^{*} + N(^{4}S) + Ar + N(3^{2}P)$$
, (22)
 $N(3^{2}P) + N(^{2}D, ^{2}P) + h\nu(149, 174 \text{ nm})$ (Ref. 46).
(23)

N atom emission at 149.2 nm was detected from the reactions of Ar^* with NO and NO₂ with comparable intensities, further evidence, in conjunction with the high O-atom yield, for the importance of channel (19). (It should be noted that no such emission was detected in the absence of reagent; however, the N line is observed if less pure Ar is used, via dissociation of impurity N₂ to N atoms in the dc discharge.)

This section of the discussion, dealing with observed branching fractions for dissociation, is completed by consideration of the reactions of Ar^* with H_2 and N_2 . In analyzing the H_2O results, it was assumed that H_2 is dissociated with unit efficiency. Accessible excited states of H₂ are the repulsive $H_2(b^3\Sigma_u^*)$ and the bound $B^{1}\Sigma_{\mu}^{*}$ state, emission from which is extremely weak and has been ascribed to the reaction of H_2 with the resonant state $Ar({}^{3}P_{1})$. 47,48 Two further states of H_{2} lie just above the energy of $Ar({}^{3}P_{0})$, the metastable $c{}^{3}\Pi_{u}$ state and the $a^{3}\Sigma_{s}^{*}$ state, emission from which to $b^{3}\Sigma_{u}^{*}$ accounts for about 5% (this study) to 10% (Ref. 32) of the reaction. Because of the small yield of $a^{3}\Sigma_{g}^{*}$, it is expected that that of $c^{3}\Pi_{u}$, which has a very similar potential curve, will not be much greater. Thus, the only possible alternative to dissociation is vibrational excitation of ground state H₂, which, by analogy with all the other quenching molecules studied here, is expected to be unimportant.

It is interesting to apply the results of this study to the reaction of $Ar({}^{3}P_{0,2})$ with N₂. Although the bond energy of N₂(9.75 eV) makes dissociation possible, no evidence for N atom formation has been reported and only two channels appear to be important

$$Ar^* + N_2 - N_2(C^3 \Pi_u) + Ar , \qquad (24)$$

$$\rightarrow N_2(B^3\Pi_g) + Ar . \qquad (25)$$

Much controversy exists over the relative branching fractions for these channels, an early discharge-flow study¹⁶ favoring channel (25) over channel (24) by a factor of 6, whereas a beam study 49 found no evidence of $B^{3}\Pi_{g}$ formation. In a recent flow study, ³² cascade formation of the B state by (C - B) emission was carefully allowed for, and it was concluded that primary formation of the B state occurs dominantly into v = 0, and that this accounts for about 40% of the reaction. This highly specific process, involving an energy mismatch of more than 4 eV, contrasts markedly with the findings of the present study, in which no significant formation of low lying states of the parent molecule is found. As the branching fraction of 0.6 for channel (24) was assigned an uncertainty of only 15%, it seems possible that a further channel exists. Therefore, we tested for N atoms in the way described above for NO and NO_2 . N atom emission was found and it is estimated 50 that 20% $\pm 10\%$ of the reaction occurs via dissociation. The magnitude of the emission intensity precludes the possibility that the N atoms arise via a secondary process, such as energy pooling of metastable $N_2(A)$ molecules, which are the cascade products of molecules formed

initially in the $N_2(B)$ or $N_2(C)$ states. Following this experiment, a further measurement³³ of channel (24) was published, yielding a branching fraction of unity. As both recent determinations^{32,33} appear equally valid, but both are possibly subject to systematic errors of at least 20%, we suggest that the best presently available branching fraction is 0.8 ± 0.2 , consistent with dissociation as the principal competing channel. These results suggest that N_2 does in fact fit into the pattern established by the other reagents and that direct formation of $N_2(B)$ is a rather minor channel.

B. The atomization channel

The most surprising result of this work was the observation of atomization of H_2O in collisions with Ar^{*} and Kr^{*}. The allowed atomization reactions of Ar^{*} with the triatomic molecules studied here are

$$Ar^* + H_2O \rightarrow Ar + 2H + O + 2.0 \text{ eV}$$
, (26)

 $Ar^* + NO_2 \rightarrow Ar + N + 2O + 1.9 \text{ eV}$, (27)

$$Ar^* + SO_2 - Ar + S + 2O + 0.5 eV$$
, (28)

$$Ar^* + N_2O - Ar + 2N + O + 0.1 \text{ eV}$$
, (29)

the exothermicities referring to reaction of $\operatorname{Ar}({}^{3}P_{2})$. As discussed above, indirect evidence favors channel (27) as at least a minor channel for the reaction with NO₂. The O-atom yield from Ar* + SO₂ is consistent with simple fragmentation to SO+O, but, again, two pieces of evidence suggest that atomization [channel (28)] may also be occurring. Firstly, emission from SO($A^{3}\Pi$), albeit weak, extends fully to the dissociation limit. Secondly, a preliminary search for S atoms via secondary excitation by Ar* has revealed atomic S emission lines throughout the vacuum UV. More detailed studies are needed to distinguish firmly between S+O₂ and S+2O formation and to obtain branching ratios.

For $Ar^* + N_2O$, the predominance of $N_2(B)$ formation precludes channel (29) as a major channel, in accord with its very small exothermicity.

C. Mechanisms of quenching

A detailed discussion of the mechanisms of quenching is hindered by a lack of information concerning relevant potential surfaces. Nevertheless, it is of interest to consider the possible mechanisms, which could explain the great differences in the reactions of Ar* with, for instance, N₂O, which gives predominantly $N_2(B^3\Pi_e) + O$, and NO_2 , which yields appreciable quantities of NO in the $X^2\Pi$, $A^2\Sigma^*$ and $B^2\Pi$ states as well as N + 2O. The principal models that have been invoked to explain rate constants and product distributions from the reactions of excited atoms are: energy transfer via long-range multipole interactions, energy transfer via curvecrossing of entrance and exit surfaces, and reaction via an intermediate, for instance of a charge-transfer nature, which may be sufficiently long-lived for statistical models to be applicable.

In the long-range model, rate constants as high as the collision number cannot be generally obtained, unless the transitions of the species-quenching of the excited atom and excitation of the collision partner-obey dipole selection rules. This clearly reduces the likelihood of its usefulness to metastable noble gas atoms and the observed excitation channels also do not in general match the photolysis products. For instance, triplet state products are often observed, such as $N_2(C^3\Pi_u)$ from N₂ and H₂($a^{3}\Sigma_{g}^{*}$) from H₂, showing that spin conservation is the more important factor for these reactions. For CO_2 , the yield of $O({}^1S)$ is low, in contrast to the high yield from photolysis between 105 and 110 nm.⁵¹ Furthermore, the atomization channel, observed for H₂O, is apparently not important in photolysis by photons of comparable energy.⁵²⁻⁵⁴ Finally, photodissociation of NO at 107 nm causes photoionization⁵⁵ with a yield of ~ 0.70 , in contrast to the lower chemi-ionization branching fraction of 0.28 found³⁷ in the reaction of Ar* with NO.

Curve-crossing models for energy transfer from A* to BCD require crossing of potential surfaces correlating with $A^* + BCD$ (or $A^* + BCD^*$ if charge transfer has taken place) and the product surfaces, correlating with A+BCD*. In the reactions studied here, BCD* dissociates or predissociates to yield products, e.g., $B+CD^{\boldsymbol{*}}, \mbox{ and thus }BCD^{\boldsymbol{*}}\mbox{ may be populated initially at }$ an energy well above that of the asymptote. In addition, there may be repulsion between A and BCD* in the nascent A. BCD* intermediate, so that it is difficult to predict the dissociation products on energetic arguments alone. However, in general terms, if the entrance surface is flat or purely repulsive, crossing can occur only with surfaces leading to products with energies close to that of the reagents, unless the product surfaces are strongly repulsive. But, if the entrance surface is strongly attractive, then there is an enhanced probability of intersections with several product surfaces, including those with considerably lower energies in the asymptotic region.

Another possible outcome of approach on an attractive surface is a long-lived intermediate (A. BCD)*, which decays statistically to all the product states accessible from the intermediate with its particular energy. In this case, several electronic states of the products B + CD are expected and broad vibrational distributions may be found, in contrast to the direct curve-crossing model, where narrower vibrational distributions, possibly related to Franck-Condon factors for vertical excitation of the CD fragment, would be expected.

A widely-proposed attractive surface for excited atom-reagent interactions is provided by the chargetransfer model. In the simplest form of this model, ⁵⁶ the covalent A* + BCD and ionic A* + BCD⁻ surfaces cross at an A - BCD separation R_c , given by

$$R_c = e^2 / (I. P. - E.A.),$$
 (30)

where I.P. is the ionization potential of A* and E.A. is, most simply, the vertical electron affinity of BCD. When the reagents approach within R_c , an electron jump causes transfer to the attractive (Coulombic) ionic surface, allowing many intersections with possible exit surfaces. The reaction cross section according to this model is

	Electron affinity (eV) ^a		<i>R</i> _c (Å)⁵	$\sigma_{CT}(\text{\AA}^2)^{c}$	σ _Q (Ų) ^d
Reagent	Measured (reference) Derived				
H ₂	v: -3 ± 1 (63)		2.0	13.	3.6
CO	v: $-1.6 \pm 0.4(63)$		2.5	19	2.3
O ₂	ad: 0.44(64)	v: 0 ± 0.1	3.4	36(46)	35
NO	ad: 0.024(65)	v: -0.4 ± 0.1	3.1	31(37)	36
NO_2	ad: 2.36(66)	v: ∼ 2.0 ^e	6.5	130(190)	•••
SO_2	ad: 1.10(67)	v: $\sim 0.9^{\text{f}}$	4.4	61(68)	126
H ₂ O		v: < 0	< 3.4	< 37	67
N ₂ O	ad: 0.22; v: -2.2(68)		2.3	16(41)	81
CO_2	ad: -0.6(69); v: -3.5(70)		1.9	11(28)	97
ocs	ad: 0,5(69); v: -1.2(71)		2.7	22(48)	155

TABLE V. Comparison of charge-transfer and total quenching cross sections for reactions of Ar*.

^av: vertical; ad: adiabatic.

^bCalculated from Eq. (30), using vertical electron affinities.

^cCalculated from Eq. (31). Values using adiabatic electron affinities in parenthesis.

^dReference 1.

^eUsing data from Ref. 66.

^fUsing data from Ref. 67.

 $\sigma_{CT} = \pi R_c^2 \quad . \tag{31}$

The strongest evidence for the applicability of this model to reactions of metastable atoms was the discovery of the atom-transfer channel for noble-gas halide excimer formation^{57,58} [Eq. (3)] as the excimer state is largely ionic in character⁵⁹ and the dynamics and cross sections of the reactions of A* with halogen molecules are similar to those of the analogous ground-state alkali atom reactions.^{1,19,20,60} For most of the reagents studied here, no comparison with alkali reactions is possible, but σ_{CT} can be estimated from Eqs. (30) and (31), for those reagents whose electron affinities are known. In several cases, only adiabatic electron affinities have been measured⁶¹; these would be appropriate only if the molecule distorts suitably during the electron jump. For this analysis, vertical electron affinities have been estimated using spectroscopic constants, where available.⁶² The results and the measured quenching cross sections for reactions of Ar* are listed in Table V. Despite the simplicity of the model and the uncertainties in the electron affinities, several conclusions can be reached. For H_2 and CO, the model is clearly not applicable. R_c is so small that repulsive forces are operative. Even if charge-transfer takes place, it is very unlikely that the ionic curve is very attractive in this region and low energy product surfaces would not be accessible. For O_2 and NO, σ_{CT} and σ_Q are very similar, so that it is possible that charge transfer occurs and is important in determining the products of the quenching process. The charge transfer mechanism has been invoked recently for the quenching of $Na^*(3^2P)$ by NO and O_2 , ⁷² and of Cd*(¹P) by NO.⁷³ In comparison with Na* and Cd*, Ar* has a larger ionization potential, and thus smaller values of R_c , so that it is possible that repulsive forces are active in the Ar* reactions but not in those of Na*. Indirect evidence against charge

transfer as the *sole* mechanism for $Ar^* + NO$ quenching has been adduced from the observation of chemi-ionization with a branching fraction of about 0.28, analogy with the reactions with NO₂, Cl₂, and Br₂ being taken to imply that chemi-ions $(Ar + Q^* + e^-)$ are not favored end products once charge transfer to $Ar^{+}Q^{-}$ has taken place.³⁷ Thus, Ar* + NO may offer the interesting case of two competing channels, one involving charge transfer, the other not. The value of σ_{CT} for Ar* + NO₂ is very large and, although a quenching cross section is not available, it is very likely that charge transfer is dominant. ArO* formation is not exothermic, but ionization, though exothermic, is not observed and dissociation of NO2 is the major product. The diversity of products, including NO in the $X^2\Pi$, $A^2\Sigma^+$, $B^2\Pi$, $D^2\Sigma^+$, and $B'^2\Delta$ states as well as N+O+O, is consistent with access from the strongly attractive ionic potential. A rich vibrational distribution is observed in several of these states, with v = 0rarely dominant $\left[except in NO(B) \right]$, where vibrational relaxation is possible under our conditions] and this would make an interesting subject for calculations, to try to distinguish a direct reaction from complex formation.

For the other reagents, N₂O, CO₂, OCS, H₂O, and SO₂, σ_{CT} , although not negligible, is considerably smaller than σ_Q . Either quenching takes place at separations larger than R_c , or another attractive nonionic potential acts on the reagents at long range to draw them to closer range for reaction to occur: in this case, charge transfer is not an essential part of the quenching mechanism. The strongest interactions are likely to be those with H₂O and SO₂; for SO₂, σ_{CT} is large and may dominate the mechanism; for H₂O, *ab initio* calculations⁷⁴ of the interaction with Ne* show a strongly attractive potential for $C_{2\nu}$ approach of the atom towards the oxygen end of the H₂O molecule. Here, H₂O acts as a Lewis *base* and similar attractive potentials are expected for all such electron donors. In agreement with the expectation of an attractive potential, several quenching channels are seen for $Ar^* + SO_2$ and H_2O , including low-lying channels leading to ground-state SO and OH. Atomization of H₂O by Ar* gives evidence of an efficient, high-energy pathway to surfaces of H₂O, which correlate with repulsive or predissociating states of OH and/or H_2 . The latter include the repulsive first excited state $H_2(b^3\Sigma_u^*)$ and the former include the $OH(A^2\Sigma^+)$ state, whose lowest two vibrational levels are largely stable (up to $N \sim 26$ in v = 0 and $N \sim 17$ in v = 1) and contribute emission, equivalent to about $28\% \pm 9\%$ of the overall reaction. The published rotational and vibrational distributions⁷⁵ can be used to define rotational and vibrational temperatures of 2050 and 1750 K, respectively, from which the initial extent of population of higher, predissociated levels of the OH(A) state can be estimated. This suggests a large initial branching ratio for OH(A) formation of 0.52, predissociation of levels $v \ge 2$ and of high rotational levels of v = 0, 1 (a minor contribution) accounting for about one-half of the yield of O + 2H.

The weakest interactions are thus expected for CO_2 , N₂O, and OCS. For N₂O, formation of N₂($B^{3}\Pi_{e}$) has been found to be dominant, which is possibly consistent with the absence of a strongly attractive entrance channel. However, the major channel for OCS appears to be the low energy route to $CO(X) + S({}^{3}P)$, with ionization accounting also for 30% of the reaction. The higher energy of the repulsive surface correlating with CO+S may be due to the fact that it also correlates with the much higher energy limit of $O({}^{3}P) + CS(X^{1}\Sigma^{+})$. Alternatively, charge-transfer may be important, especially if OCS can bend as Ar* approaches.

Ar* + CO₂ is interesting in that formation of $CO(a^3\Pi)$ is remarkably efficient, branching ratio: 0.16, considering the weak exothermicity of this process. However, the rest of the reaction occurs efficiently to $CO(X^1\Sigma^*) + O(^3P, {}^1D)$, which is less easy to understand on the basis of the simple considerations employed here.

An implication of the approach taken here is that efficient quenching of different excited atoms by a given reagent molecule need not be expected to give identical products. Striking examples of this can be found by comparing the efficient quenching of Na(3^2P), excitation energy 2.1 eV, and of Cd(1P_1), at 5.4 eV, with Ar(${}^3P_{0,2}$). For Na^{*}, electronic-to-vibrational energy transfer is dominant.⁷² For Cd(1P_1), deactivation to Cd(3P_J) appears to be the major channel for CO, NO, and several hydrocarbons.⁷⁶ These findings suggest that the quenching mechanisms for Ar(3P_0) may differ from those of the lower-lying Ar(3P_2) state and experiments to probe such differences are underway.⁷⁷

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