Electronic energy transfer in rare gas mixtures

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(Received 20 February 1973)

In this paper we present the results of an experimental study of electronic energy transfer in xenon–argon and xenon–krypton gaseous mixtures excited by an α source. Spectroscopic evidence is presented for molecule-atom energy transfer from $Ar^*_2(^{1,3}\Sigma_u)$ to $Xe(^1P_1)$ and from $Kr^*_2(^{1,3}\Sigma_u)$ to $Xe(^3P_1)$. These two electronic energy transfer processes are characterized by large $\sim 10^{-14} - 10^{-13}$ cm^2 cross sections. Information has been obtained for collision-induced energy conversion processes of the Xe energy acceptor involving $^1P_1 \rightarrow {}^3P_1$ conversion and the formation of $Xe^*_2(^{1,3}\Sigma_u)$ at moderately low (≤ 200 ppm) Xe concentrations. A new emission band, observed in the xenon–krypton system, peaking at 1530Å, is tentatively assigned to a heteronuclear (KrXe)* diatomic molecule.

I. INTRODUCTION

Previous work[1] from this laboratory reported energy transfer from diatomic homonuclear rare gas molecules, to a rare gas atom of a different kind. These studies were based on the measurement of the vacuum ultraviolet emission spectra of rare gas mixtures, excited by an electric discharge. This excitation technique is limited to the gas phase and results in emission from a high temperature plasma. In the present work we report the results of an experimental study of energy transfer phenomena in xenon–argon and xenon–krypton mixtures excited by an α-source. This technique was previously applied[2] in the study of the emission spectra of pure rare gases. The goals of the present work are:

(a) To obtain detailed information concerning the electronic states involved in the energy transfer process between rare gas diatomics and rare gas atoms. This information has been only indirectly obtained in our previous work.[1]

(b) To investigate collision induced energy conversion processes of the energy acceptor.

(c) To gain further insight into the formation mechanism of rare gas diatomic molecules.

II. EXPERIMENTAL TECHNIQUES

The experimental setup consists of three subsystems: (a) a cryogenic cell with an incorporated α-source; (b) a McPherson 218 0.3M-Czerny–Turner monochromator; (c) a photodetection and recording system. The cryogenic cell and its gas feeding vacuum system have been previously described.[3] In this particular experiment the back window of the optical cell (path length 1 cm) was replaced by an ^{241}Am 0.5 m-Curie α-source. The cell was mounted on a nitrogen flow cryostat, adjustable in the temperature range 300 to 80°K to within ± 0.1 °K. A purity check of the cryogenic cell and of the gas supply vacuum system was per-

formed by monitoring the emission spectra of pure argon and pure krypton. The results shown in Fig. 1 indicate that the gas handling procedure is adequate and that the impurity content of the argon gas (Matheson research grade) was below tolerable limits ($\lesssim 1$ ppm). The emission spectrum of "pure" krypton (Matheson research grade Xe impurity content ~10 ppm) exhibits the emission of the Xe impurity. The photodetection system consisted of a 9514S EMI photomultiplier which was cooled down to −70°C, and its dark current at this temperature was about 2×10^{-10} A. The combination of the low intensity excitation source and the detection system, determined the spectral resolution which was between 13 and 26 Å.

III. EXPERIMENTAL RESULTS

In Fig. 2 we present the spectra of xenon–argon mixtures at 1000 torr argon.[4] Three different emission bands are observed. At low partial pressures (< 75 ppm) of xenon the resonance emission lines of atomic xenon (at 1296 Å from the $^1P_1$ state and at 1470 Å from the $^3P_1$ state)[5] are observed. At somewhat higher partial pressures of Xe a third broad band emission appears, peaking at 1720 Å. This broad band is due to emission from the molecular $^3\Sigma_u$ or $^1\Sigma_u$ state of the Xe^*_2 molecule to the (repulsive) ground state.[6]

The intensity ratio of the atomic bands at 1296 and at 1470 Å depends on Xe concentration. The 1296 Å ($^1P_1 - {}^1S_0$) emission is prominent at the lowest Xe concentrations and is attenuated in favor of the 1470 Å ($^3P_1 - {}^1S_0$) emission with increasing Xe density.

The emission spectra of xenon–krypton mixtures are presented in Fig. 3. A broad emission band is observed at 1480 Å, and assigned to the $^{3,1}\Sigma_u - {}^1\Sigma_g$ transition of the Kr^*_2 molecule, which acts as the energy donor in this system. The atomic ($^3P_1 - {}^1S_0$) emission at 1470 Å and the Xe^*_2 molecular ($^{3,1}\Sigma_u - {}^1\Sigma_g$) emission at 1720 Å were observed
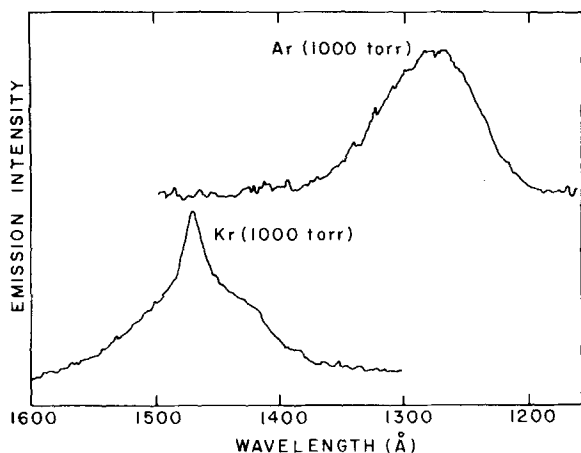
FIG. 1. Emission spectra of "pure" gaseous argon and krypton. At room temperature the Ar spectrum does not exhibit any impurity emission while the Kr spectrum reveals the Xe line at 1470 Å.

as in the Xe/Ar system. Still another broad emission is observed, peaking at 1530 Å. This band is of particular interest, as it has no counterpart in the Xe/Ar system, in pure Kr, or in pure Xe. We tend (see Sec. IV.D) to assign this emission band to a heteronuclear excited diatomic (XeKr)* molecule. Another interesting feature of the spectra
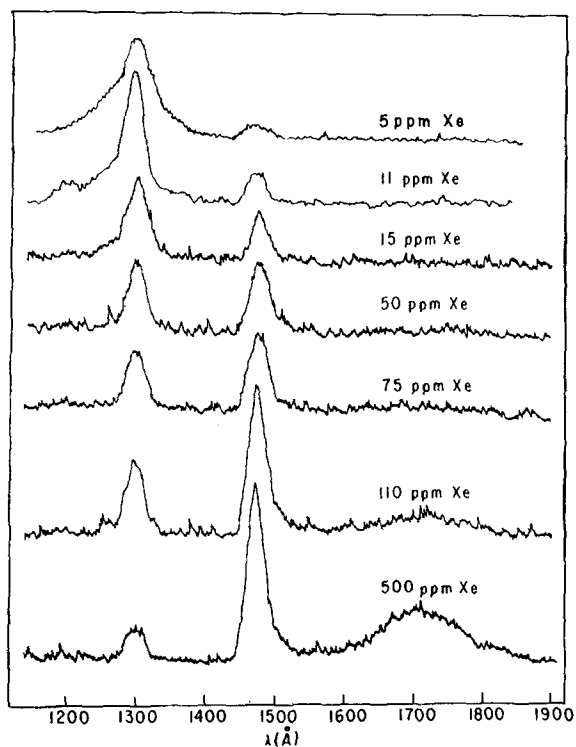

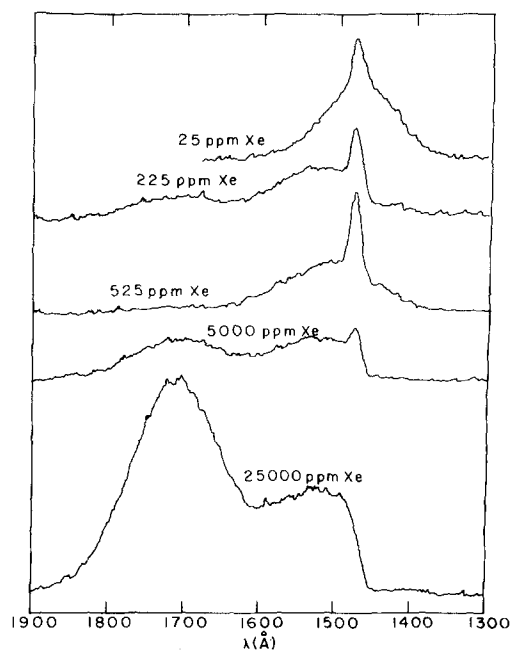FIG. 2. Emission spectra of gaseous argon (1000 torr) doped by Xe at room temperature (resolution 25 Å).

FIG. 3. Emission spectra of gaseous krypton (1000 torr) doped with Xe at room temperature (resolution 13 Å).

exhibited in Fig. 3 is the total absence of the Xe ($^1P_1 - {}^1S_0$) atomic emission at 1296 Å.

The experimental results presented herein should be analyzed from two points of view:

(a) Analysis of the collision-induced processes of the energy acceptor in its excited states.

(b) Estimates of cross sections for the energy transfer processes from diatomic Ar_2^* and Kr_2^* molecules to atomic Xe.

IV. DISCUSSION

A. Molecule-Atom Energy Transfer

Previous work[1] advanced two mechanisms for electronic energy transfer in rare gas mixtures. Energy transfer to the acceptor atom can occur from (a) an excited (metastable) donor atom; (b) an excited homonuclear molecule in the $^3\Sigma_u$ and $^1\Sigma_u$ states (which originates from the $^3P_2 + {}^1S_0$ and from the $^3P_1 + {}^1S_0$ atomic configurations, respectively). Mechanism (a) operates at moderately low pressure of the donor.[1] On the basis of previous work we can infer that in Ar and Kr mixtures at 1000 torr mechanism (b) will dominate. The molecule-atom energy transfer processes are

$$(^{1,3}\Sigma_u) + (^1S_0) \Big\langle \begin{array}{l} (^1P_1) \text{ for Xe/Ar} \\ \\ (^3P_1) \text{ for Xe/Kr} . \end{array}$$
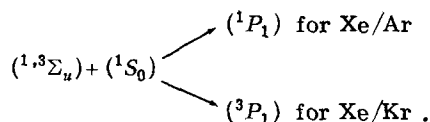
From the spectroscopic data summarized in Figs. 2 and 3 and in Table I we conclude that in the Xe/Ar systems the $^1P_1 - {}^1S_0$ acceptor emission is prominent at low Xe densities while in the Xe/Kr system the only atomic transition observed involves the $^3P_1 - {}^1S_0$ emission of the acceptor. The $^1P_1$ state of Xe overlaps the $^3\Sigma_u$ and the $^1\Sigma_u$ excited molecular levels of Ar_2^*, making it a perfect energy accepting level in the molecule-atom transfer process. On the other hand, the $^3\Sigma_u$ and $^1\Sigma_u$ levels of Kr_2^* overlap the Xe $^3P_1$ state, but no such level coincidence occurs with the Xe $^1P_1$ state. The observations summarized in Table I and especially the total absence of the $^1P_1 - {}^1S_0$ emission in the Xe/Kr system are considered by us to provide a proof for a resonant molecule-atom energy transfer in these systems, excluding the effects of atom—atom transfer or of a direct excitation mechanism.

B. Xe_2^* Molecular Emission in Xe/Ar and Xe/Kr

At finite but still low Xe concentrations (~200 ppm Xe in Kr and in Ar at total pressure of 1000 torr) we have observed a broad emission peaked at 1720 Å. This emission band coincides in energy and in its half linewidth with the emission spectrum of pure Xe (at $p \sim 100$ torr),[7] and is assigned to the $^{3,1}\Sigma_u - {}^1\Sigma_g$ decay of the Xe_2^* molecule. The formation of homonuclear rare gas diatomics at low partial pressure in the presence of a high pressure of a buffer rare gas has been previously observed in this laboratory[1] in the Xe/Ar system. This effect was interpreted by us[1] in terms of a collision-induced deactivation of Xe ($^3P_1$) resulting in the formation of the metastable Xe ($^3P_2$) state which recombines (through a three body collision) with a ground state Xe ($^1S_0$) atom to yield the excited Xe_2 ($^3\Sigma_u$) molecule.

C. Xe ($^1P_1$) → Xe ($^3P_1$) Conversion in the Xe/Ar System

In Fig. 4 we present the relative intensities of the three acceptor emissions in the Xe/Ar system (i. d., Xe atom $^1P_1 - {}^1S_0$, $^3P_1 - {}^1S_0$ transitions and Xe_2 $^{3,1}\Sigma_u - {}^1\Sigma_g$ transitions) plotted against the partial pressure of Xe (at constant Ar pressure). As the Xe concentration increases the intensity of the $^1P_1 - {}^1S_0$ emission decreases, with the simultaneous increase in the emission intensities of the Xe $^3P_1 - {}^1S_0$ and the Xe_2^* $^{3,1}\Sigma_u - {}^1\Sigma_g$ transitions. This in-

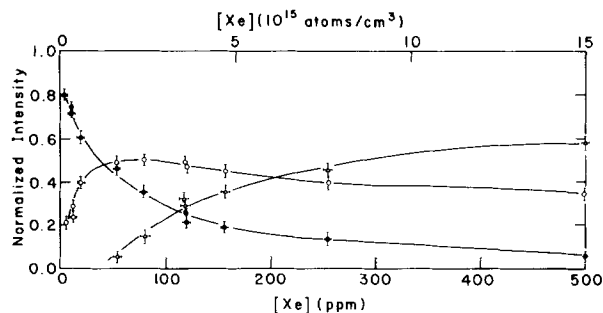FIG. 4. The fractional intensity of the three acceptor emissions in the xenon/argon system. ● –intensity of the atomic transition $^1P_1 - {}^1S_0$; ○–intensity of the atomic transition $^3P_1 - {}^1S_0$; △–intensity of the molecular Xe_2^* transition $^{1,3}\Sigma_u - {}^1\Sigma_g$.

tensity dependence in Fig. 4 is reminiscent of a consecutive collision-induced process which can be qualitatively rationalized as follows: (a) The conversion of the initially populated Xe ($^1P_1$) state to the Xe ($^3P_1$) state involves a collision-induced excitation with an Ar atom to a Xe ($^3D_1$) state located 84 cm^{-1} above the Xe ($^1P_1$) level[5] (see Fig. 5). The Xe ($^3D_1$) state decays radiatively to the lower Xe ($^3P_1$) and Xe ($^3P_2$) levels. (b) The efficiency of the Xe ($^1P_1$)→Xe ($^3P_1$) conversion process depends on the partial pressure of Xe. This concentration dependence originates from radiation trapping effects[8] which increase the effective radiative lifetime of the Xe ($^1P_1$) state and thus enhance the branching ratio for the Xe ($^1P_1$)→Xe ($^3D_1$) thermal activation process. The linear dependence of the Xe ($^1P_1$)/[Xe ($^3P_1$)+Xe_2^*] intensity ratio on [Xe] (see Fig. 6) is in qualitative agreement with the prediction of Holstein's theory[9] of resonance trap-

TABLE I. Peaks of emission band in Xe/Ar and in Xe/Kr systems.

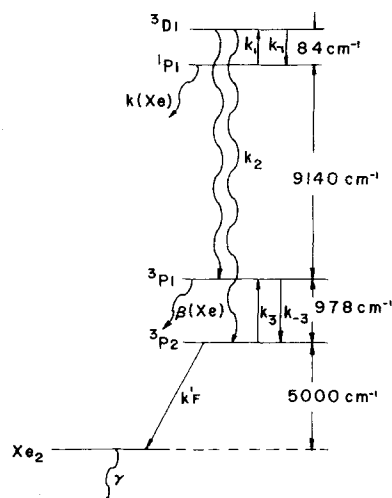| System \ Energy level	Donor $^{3,1}\Sigma_u - {}^1\Sigma_g$	Acceptor $^1P_1 - {}^1S_0$	$^3P_1 - {}^1S_0$	Molecule (?)	$^{3,1}\Sigma_u - {}^1\Sigma_g$
Xe/Ar	1300 Å	1296 Å	1470 Å	···	1720 Å
Xe/Kr	1480 Å	···	1470 Å	1530 Å	1720 Å

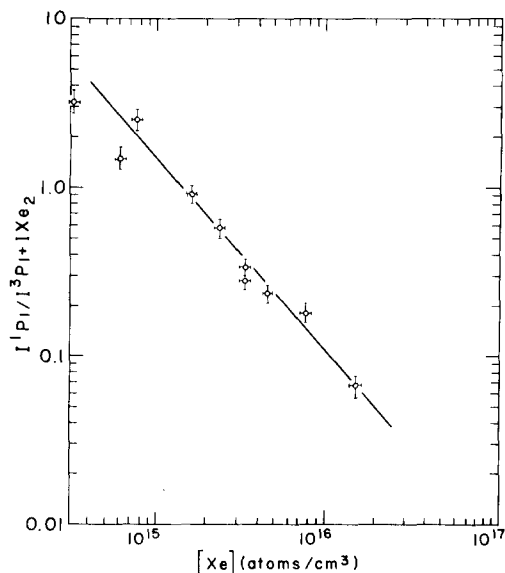FIG. 5. A schematic presentation of the energy levels for the Xe ($^1P_1$) →Xe ($^3P_1$) conversion.

FIG. 6.   The intensity ratio I (Xe $^1P_1$)/[I (Xe $^3P_1$) + I (Xe$_2^*$)] as a function of Xe concentration in the xenon argon gaseous mixtures.

ping.   Radiation trapping experiments on the $^3P_1$ $\rightarrow ^1S_0$ transition in Hg[10] exhibits a similar density dependence.   The present data cannot be quantitatively compared with the predictions of Holstein's because of two reasons.   First, the distribution of the excited atoms is not homogeneous under our experimental excitations conditions; second, our experiments were performed at moderately high Ar pressures where no detailed information is available on the Xe* emission lineshapes.   Nevertheless, our experimental data provide qualitative evidence concerning the crucial role of radiation trapping effects on the Xe ($^1P_1$)→Xe ($^3P_1$) conversion process.

The Xe ($^3P_1$) state thus formed can be deactivated into the metastable Xe ($^3P_2$) state, which at relatively low Xe pressure (see Sec. IV.B) forms a Xe$_2^*$ ($^3\Sigma_u$) molecule.   It should be stressed that the present results provide further evidence for the formation of homonuclear rare gas diatomics via an atomic rather than by an ionic mechanism.

D. A Conjecture on a Heteronuclear Rare Gas Molecule

While the spectroscopic assignment of all four emission bands observed in the Xe/Ar system is quite obvious, the Xe/Kr system exhibits a broad emission band peaking at ~1530 Å, the interpretation of which is by no means straightforward.   The intensity of the 1530 Å band depends linearly on the Xe pressure and thus it has to be assigned to a molecular species which contains at least one Xe atom.   One could argue that the 1530 Å emission originates from the first continuum[6] of the Xe$_2^*$

($^{1,3}\Sigma_u$) molecule which is formed in the Xe/Kr system.   This interpretation is rejected on the basis of two arguments.   First, no analogous emission was observed from the Xe/Ar system at identical pressure.   Second, the 1530 Å band is observed in Xe/Kr at a Kr pressure of 1000 torr and it is expected that under these conditions collision-induced vibrational relaxation in the Xe$_2^*$ molecule should be efficient.

A possible assignment of the 1530 Å emission involves an excited ionic molecule XeKr*.   Some evidence against this possibility is based on the observation of an analogous emission (peaked at ~1560 Å)from Xe impurity excited states in solid and in liquid krypton.[11]   In these dense phases electronic mobility is extremely high[12] (10^3 cm$^2 \cdot$ V sec^{-1}) and electron–ion recombination process are efficient so that emission will originate from neutral rather than from ionic molecules.

We tentatively assign the 1530 Å emission in the Xe/Kr system to a heteronuclear excited XeKr* diatomic molecule.   The observation of an analogous emission in Xe/Kr (solid) and Xe/Kr (liquid) supports this assignment.   Independent evidence for the existence of the excited (XeKr)* molecule was introduced by Friede[13] who had observed a new emission band (4600–4950 Å) in the visible emission spectra of Kr/Xe mixtures excited by fast electrons (50 keV), which has no parentage in the spectra of pure Kr or Xe gases.   This band was assigned to a (XeKr)* excited molecule.

E. Cross Sections for Electronic Energy Transfer

An approximate theoretical scheme for the molecule–atom energy transfer in rare gas mixtures was outlined in our previous work[1] and we present here the final results of a slightly refined version of the theory.   The energy transfer cross section, σ, and the kinetic bimolecular rate constant, k_{ET}, are expressed in the form

$$\sigma = (2\pi/5)[-\Gamma(2/5)] (3W_{rad}R_q^6/8\langle v \rangle)^{2/5}, \quad (\text{IV. 1})$$

$$k_{ET} = \sigma \langle v \rangle, \quad (\text{IV. 2})$$

where W_{rad} is the radiative decay probability of the diatomic donor molecule, $\langle v \rangle$ is the mean relative velocity of the donor-acceptor pair, while R_q represents the transfer radius, the distance where the branching ratio between the nonradiative energy transfer and the radiative decay probability is unity.

$$R_q = (\lambda^3\mu_A^2 F(E_A)/8\pi^2)^{1/6}, \quad (\text{IV. 3})$$

where μ_A is the transition moment of the atomic energy acceptor, λ is the (mean) wavelength for the molecular donor emission, while $F(E_A)$ is the (normalized) lineshape function for the molecular emis-

sion at the energy $E = E_A$ which corresponds to the electronic excitation of the atomic energy acceptor.

All the molecular and atomic parameters which determine R_q are reasonably well known. For electronic molecule–atom energy transfer to the Xe ($^1P_1$) state in the Xe/Ar system and to the Xe ($^3P_1$) state in the Xe/Kr systems E_A practically coincides with the maximum of the corresponding molecular emission band. Approximating $F(E)$ by a rectangular intensity distribution results in $F(E_A) = 2 \times 10^{-4}$ cm for both systems. For an allowed atomic transition of the energy acceptor we take $\mu_A = 1$ Debye for the $^1S_0 \rightarrow {}^3P_1$ and the $^1S_0 \rightarrow {}^1P_1$ transitions. Thus from Eq. (IV. 3) we get $R_q = 17$ Å for Xe/Ar and $R_q = 19$ Å for Xe/Kr. The energy transfer cross section is determined by R_q and by the radiative decay probability of the diatomic energy donor. The energy transfer cross sections from the $^3\Sigma_u$ and from the $^1\Sigma_u$ molecular states may vary appreciably in view of their different radiative lifetimes. The radiative decay times τ_1 and τ_2 of the $^1\Sigma_u$ and the $^3\Sigma_u$ molecular states, respectively, have been determined for two cases only. Colli[14] has reported the value $\tau_2 = 3.4 \times 10^{-6}$ sec for Ar$_2^*$. Recently, Koehler et al.[15] have reported $\tau_1 = 2 \times 10^{-8}$ sec for Xe$_2^*$. As the radiative decay times of the $^3P_1$ atomic states of Xe and of Kr are very close (4.38×10^{-9} sec for Kr[16] and 3.74×10^{-9} sec for Xe[17]) we assume that τ_1 (Kr$_2^*$) $= \tau_1$ (Xe$_2^*$) $= 2 \times 10^{-8}$ sec. The lifetime of the Ar$_2^*$ $^1\Sigma_u$ state is assumed to be approximately given by the relation $\tau_1(\text{Ar}_2^*)$ $= \tau_1$ (Xe$_2^*$)$[\tau(\text{Ar}_1{}^3P_1)/\tau(\text{Xe}_1{}^3P_1)]$. As the ratio of the decay times of the atomic states is $\tau(\text{Ar}, {}^3P_1)/\tau(\text{Xe}, {}^3P_1) = 5.4$[18] we estimate τ_1 (Ar$_2^*$) $\approx 10^{-7}$ sec. Finally we take the lifetime of the $^3\Sigma_u$ state of Kr$_2^*$ to be equal to τ_2 of Ar$_2^*$, so that τ_2 (Kr$_2^*$) $\approx 3 \times 10^{-6}$ sec. The theoretical estimates of the molecule-atom cross sections are summarized in Table II. The cross sections for these resonance electronic
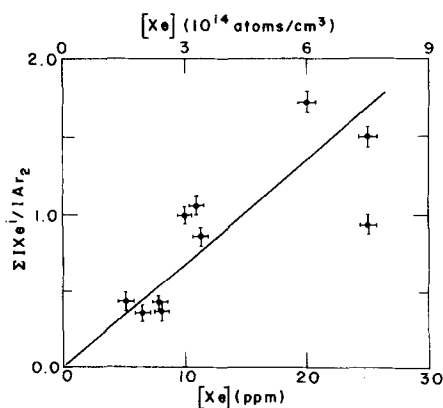
energy transfer processes are quite large ($\sim 10^{-15}$ cm^2). The present theoretical approximate treatment is expected to result in a lower limit for σ. A similar situation prevails in the case of resonance atom–atom energy transfer where the application of a semiclassical treatment results in cross sections which are smaller by about one order of magnitude than those calculated by more elaborate methods.[19]

The experimental data relevant to the determination of the energy transfer cross sections are presented in Figs. 7 and 8 where we have displayed the intensity ratio $x = I_A/I_M$ of the total acceptor

FIG. 8. The branching ratio I_A/I_M in the gaseous krypton–Xenon system as a function of xenon concentration.

FIG. 7. The branching ratio I_A/I_M in the gaseous argon–xenon system as a function of xenon concentration.

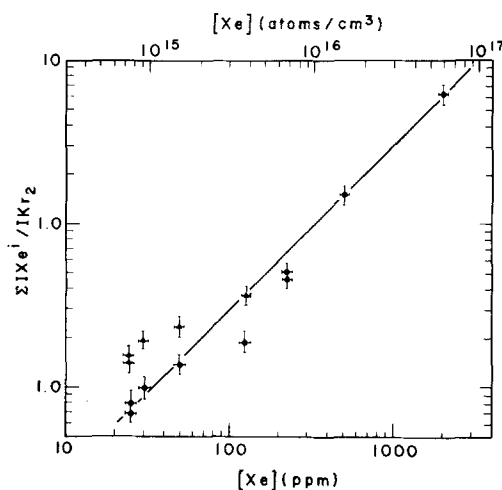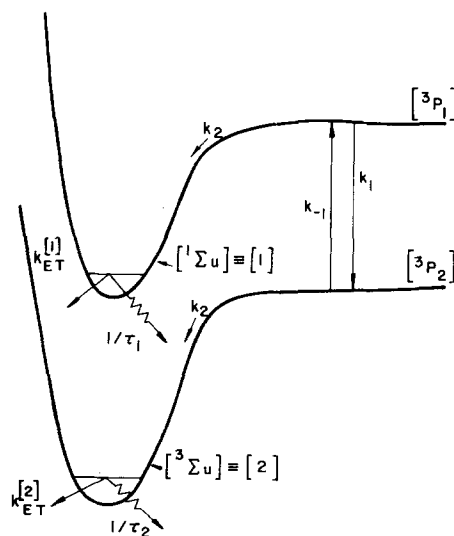FIG. 9. A schematic presentation of energy levels and rate constants concerning the formation of the homonuclear diatomic donor molecule.

TABLE II. Molecule-atom energy transfer cross sections.

System	R_q^{c*} (Å)	τ_1 (sec)	σ_1 (cm^2)	τ_2 (sec)	σ_2 (cm^2)	σ_1 (cm^2)	σ_2 (cm^2)
		Estimates of cross sections[a]				Experimental cross sections[b]	
Xe/Kr	19	2×10^{-8}	5.3×10^{-15}	3.4×10^{-6}	7.0×10^{-16}	7.8×10^{-14}	1.0×10^{-14}
Xe/Ar	17	1×10^{-7}	1.8×10^{-15}	3.4×10^{-6}	4.4×10^{-16}	3.2×10^{-13}	7.8×10^{-14}

[a] Calculated according to formula (IV. 1).
[b] From the analysis at high [Xe] data, where experimental results are more reliable.
[c] Calculated according to formula (IV. 3).

emission, I_A, and the donor molecular emission, I_M, vs the acceptor concentration. The analysis of these data is rather complicated in view of the nonspecific excitation of a two-level energy donor system. In Fig. 9 we present the relevant energy level scheme for the donor molecule. The basic energy conversion and energy transfer processes are expressed in terms of the following kinetic equations:

$$d[\,^3P_1]/dt = \alpha_1 - k_2 p^2 [\,^3P_1] - k_1 p [\,^3P_1] + k_{-1} p [\,^3P_2],$$
(IV. 4)

$$d[\,^3P_2]/dt = \alpha_2 + k_1 p [\,^3P_1] - k_2 p^2 [\,^3P_1] - k_{-1} p [\,^3P_2],$$
(IV. 5)

$$d[1]/dt = k_2 p^2 [\,^3P_1] - (1/\tau_1)[1] - k_{ET}^{(1)}[1][A],$$
(IV. 6)

$$d[2]/dt = k_2 p^2 [\,^3P_2] - (1/\tau_2)[2] - k_{ET}^{(2)}[2][A],$$
(IV. 7)

where α_1 and α_2 are the excitation rates of the majority (Ar or Kr) atoms into the $^3P_1$ and into the $^3P_2$ states, respectively; [1] and [2] represent the concentrations of the donor molecules in the $^1\Sigma_u$ and in the $^3\Sigma_u$ states, respectively; $[A] \equiv [Xe]$ corresponds to the concentration of the acceptor atoms and p is the pressure of the majority atoms. All the rate constants are defined in Fig. 9. In view of the relatively large electronic energy gap between the $^3P_1$ and the $^3P_2$ atomic states (945 cm^{-1} for Kr and 607 cm^{-1} for Ar) it is safe to assume $k_{-1} \ll k_1$. Furthermore, under our experimental conditions ($p = 1000$ torr) we assume that $k_{-1} \ll k_2 p$, this assumption being compatible with Turner's data for Kr$_2^*$.[20] Under steady state conditions we have

$$x \equiv \frac{IA}{IM} = [Xe] \frac{z \{ k_{ET}^{(2)} [Xe] + 1/\tau_2 \} k_{ET}^{(1)} + \{ k_{ET}^{(1)} [Xe] + 1/\tau_1 \} k_{ET}^{(2)}}{z \{ k_{ET}^{(2)} [Xe] + 1/\tau_2 \} (1/\tau_1) + \{ k_{ET}^{(1)} [Xe] + 1/\tau_1 \} 1/\tau_2},$$
(IV. 8)

where

$$z = \frac{(\alpha_1/\alpha_2) \{ 1 - [k_1/(k_2 p + k_1)] \}}{1 + (\alpha_1/\alpha_2)[k_1/(k_2 p + k_1)]} .$$
(IV. 9)

The energy transfer rate constants k_{ET}^{1} and k_{ET}^{2} are interrelated by Eq. (IV. 1) in the form

$$y \equiv (k_{ET}^{(1)}/k_{ET}^{(2)}) = (\tau_2/\tau_1)^{2/5} .$$
(IV. 10)

This ratio being $y = 7.8$ for Kr$_2^*$ and $y = 4.1$ for Ar$_2^*$.

Under the present experimental conditions of nonspecific excitation of the majority atoms, we do not have any information concerning the ratio α_1/α_2. From the linear dependence of x on [Xe] (see Figs. 7 and 8) two physical cases can be realized: (a) $k_{ET}^{[i]} [Xe] \ll 1/\tau_i$ or (b) $k_{ET}^{[i]} [Xe] \gg 1/\tau_i$ (where $i = 1, 2$). For low [Xe] concentrations employed herein we expect relation (a) to hold for [Xe] $\lesssim 50$ ppm and [Xe] $\lesssim 1$ ppm for the Xe/Kr and Xe/Ar systems, respectively. We made the as-

sumption that the relevant rate constants of the argon atom are the same as those of the Kr atom[18]; thus, we have solved Eq. (IV. 8) with the proper y value [Eq. (IV. 10)] for the Xe/Ar and for the Xe/Kr systems over a wide range of the ratio α_1/α_2. The calculated intensity ratio x is changed only by one order of magnitude when α_1/α_2 varies in the range 0–100. We have arbitrarily chosen $\alpha_1/\alpha_2 = 1$ and presented in Table II the estimated cross sections.

We note that the estimated molecule-atom energy transfer cross sections are exceeding high σ_1 $\sim 10^{-13}$ cm^2 and $\sigma_2 \sim 10^{-14}$ cm^2, being similar for the Xe/Ar and for the Xe/Kr systems, as expected. In spite of the one order of magnitude uncertainty in the σ values we can conclude that electronic energy transfer between rare gas molecules and a rare gas atom of a different kind is an extremely efficient process, which apart from its intrinsic interest, might prove useful for laser applications in the vacuum ultraviolet.

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