Kinetic study of energy transfer from He($n = 2, 3$) to Ne, Ar, Kr, and Xe†

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Time-resolved spectroscopic studies have been carried out on various emissions from He-Ar, He-Kr, He-Xe, and He-Ne mixtures to obtain kinetic information and quenching cross sections following charged-particle excitation. Our results are consistent with the pathways model of Payne, Klots, and Hurst in which Jesse effects are due primarily to energy transfer from He($2\,^1S$) to an atom or molecule which is consequentially ionized. Quenching cross sections for He($2\,^1S$)-Ar, -Kr, and -Xe at thermal (300°K) collision energy were obtained as 22.5, 42, and 70 Å^2, respectively, with an accuracy of 10%. These results are smaller than theoretical calculations which make use of the orbiting approximation, but agree well with experimental data obtained by crossed-molecular-beam methods. Using the same method, we obtained for the first time room-temperature quenching cross sections for He($2\,^1P$)-Ar and He($3\,^1P$)-Ne, -Ar, -Kr, -Xe (142 ± 42, 42 ± 4, 53 ± 5, 39 ± 4, and 73 ± 7 Å^2, respectively). These results are larger than theoretical calculations based on the dipole-dipole mechanism by Katsuura and Watanabe. Quenching cross sections for He($3\,^3P$)-Ne, -Ar, -Kr, -Xe, and He($3\,^1D$)-Ne were obtained as 32 ± 5, 22 ± 3, 17 ± 3, 67 ± 10, and 30 ± 5 Å^2, respectively.

I. INTRODUCTION

During the past few years, a large number of theoretical and experimental efforts have been undertaken to study energy transfer from excited rare-gas atoms. Energy transfer from excited helium atoms ($n = 2, 3$) is interesting because it is amenable to theoretical calculations, and because it has a number of timely applications in uv lasers, e.g., He-Cd and He-N_2 lasers. Phelps[1] did an extensive absorption study of the decay of He($2\,^1S$) in pure helium. He attributed the suggested collision-induced emission[2] to be due to the $A\,^1\Sigma_u^+$ molecule created by barrier penetration into a quasibound vibrational level. This interpretation was later supported by further studies.[3,4]

Recently, Payne *et al.*[5] introduced a model, based on previous data,[6] of vacuum ultraviolet (vuv) emission in He after charged-particle excitation. They suggested that at pressures between 10 and 200 Torr, much of He($2\,^1P$) is converted to He($2\,^1S$) in two-body collisions. With this model, the decay rate of He($2\,^1S$), based on the high-pressure (200–1000 Torr) data of Ref. 6 and the low-pressure (<100 Torr) data taken, using absolute populations measured by a laser technique,[7] is

$$\beta = 220P + 1.4P^2 \quad (\beta \text{ in sec}^{-1}, \text{ and } P \text{ in Torr}).$$

The $220P$ represents emission from the $A\,^1\Sigma_u^+$ ($1\,^1S + 2\,^1S$) molecule created by barrier penetration into a quasibound vibrational level. This process leads to the emission of the diffuse band in the region of 601–606 Å. The $1.4P^2$ contribution to the decay rate is due to collisional stabilization by a third body from the quasibound vibrational levels of the $A\,^1\Sigma_u^+$ molecule. The stabilized A molecule radiates the slow continuum from 601 to 950 Å.

Since He($2\,^1S$) can decay through collisional-induced emission, the time-resolved vuv method at 601 Å can be used to monitor this population in studying energy-transfer processes. When small amounts of foreign species are added to He, the vuv radiation band (601–606 Å) decays at an increased rate due to its quenching. As a result, the rates of the energy transfer can be obtained from the increase in the rate of decay, and thus this is a sensitive method for studying time-resolved quenching processes. Moreover, it is not limited to metastable state quenching; it also provides a simple way to study resonance and other short-lived states that are inaccessible to beam techniques.

The helium metastable system has been studied by a number of methods.[8] These include afterglow of pulsed helium discharges,[9] a beam gas cell technique,[10] flowing afterglow,[11] and crossed-beam methods.[12–14] The velocity dependence of the energy transfer was also treated by a number of researchers[13,15–19] who have obtained information on the interaction potentials. Theoretical aspects of Penning ionization due to energy transfer from metastable atoms have been considered as a type of autoionization of the unbound adiabatic molecular states of the colliding atoms, where the scattering is described by a local optical potential.[20] The effect of the uncertainties[21] and shape[22,23] of the potential on the ionization cross section was discussed. We note that the discrepancies amongst the above studies are significant, and no one has claimed better than 20% accuracy. The time-resolved vuv emission at 601 Å, reported in this work, provides an accurate deter-

mination (10%) of the Penning ionization cross section.

The ionization process of the optically allowed transitions of rare gases has been theoretically studied,[24-27] and expressions have been given[25] for the cross section and the reaction-rate constant which indicate insensitivity to variations in temperature. This theory[25] was recently put to test when the Penning ionization of He($3\,^1P$) with various rare gases was measured at temperature 600°K.[28] These results indicate lack of agreement with the theory. However, some previous data,[29,30] taken by the present method on energy transfer from Ar resonance states to ethylene and nitric oxide, seem to indicate good agreement with the theory, even though the conditions for validity of the theory are not clearly met.

Since our present method has had good agreement with the measurements on He($2\,^1S$) by beam techniques, and since the resonant states are inaccessible to beam techniques, we performed a series of quenching experiments which produced room-temperature rates reported here for the first time. Among these are the rates for He($2\,^1P$)-Ar; He($3\,^1P$)-Ne, -Ar, -Kr, -Xe; He($3\,^3P$)-Ne, -Ar, -Kr, -Xe; and He($3\,^1D$)-Ne.

II. EXPERIMENTAL

The schematic diagram of the experiment is shown in Fig. 1. 15-nsec pulses of 2-MeV protons are sent into the reaction cell to produce ion pairs and excited atomic states. The proton pulse can be repeated with repetition time intervals from 4–256 μsec, or it can be triggered manually. The number of protons per pulse can be varied from ~10^4 to ~10^7. The proton beam intensity was always set low enough to prevent superelastic collisions with electrons, or other nonlinear effects due to saturation of excited species. The incoming pulse of protons triggers a time-to-pulse height converter, and the pulse is stopped by the detection of photons at single photon detectors attached to vuv and visible spectrometers. The emitted vuv photons are resolved with a vuv monochromater (McPherson 235) set at 5 Å resolution during the experiment, and are detected by a Bendix channel electron multiplier (model 4219). Ultraviolet-visible photons pass through a quartz window and enter a McPherson monochromator (model EU 701). The resolution is set at 2 Å. Photons with a selected wavelength are detected with a Bendix photomultiplier (model 7500-5201), which has a dark count rate of 3 counts/sec, in normal operation. The dark count of the vuv detector is 0.3 count/sec.

Helium gas (99.9999% purity) and Ar, Kr, and Xe (research grade) were flowed through the room-temperature reaction cell for He($n=3$) experiments. A mixture of 1% of Ar or Kr or Xe in He was flowed through the flow meter and mixed with pure He(99.9999% purity) to obtain the low

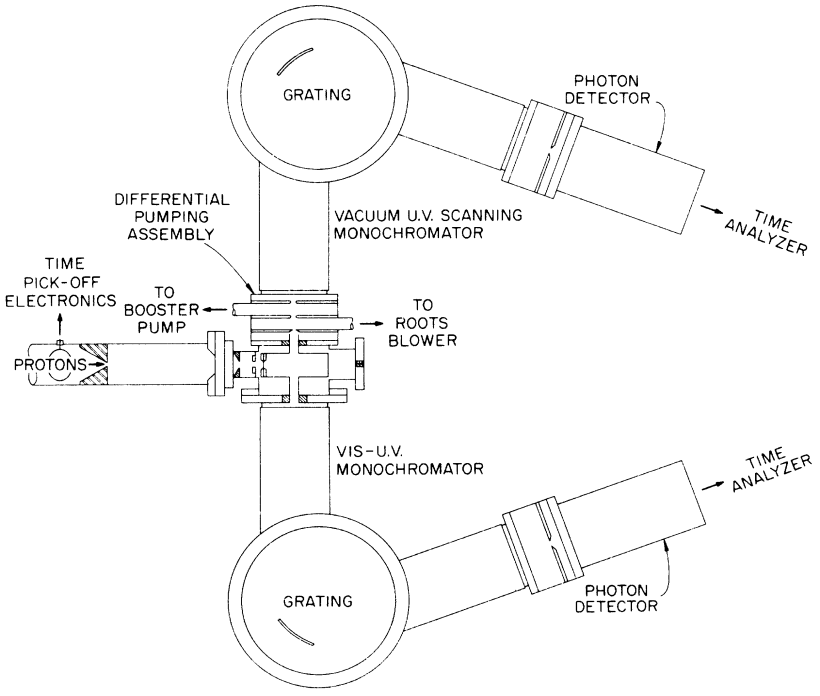

FIG. 1. Schematic diagram of experimental set-up.

concentration with a few parts per million before entering the reaction cell in He(n=2) experiments. The total pressure in the reaction cell can be read with an accuracy of 0.001 Torr with an MKS Baratron pressure gauge. The flow rate can be determined within 1% by a calibrated Hastings digital flow meter.

A technique for measuring rates of excitation transfer from spectroscopically resolved resonance states has been discussed previously.[29,30] The technique can also be extended to the study of the He singlet metastable state, because emission near 601 Å is stimulated from He($2\,^1S$) in a two-body collision process, as was discussed in the Introduction. The decay constant $\beta = \beta_P + \alpha_i P_Q$, where β_P is the pure-gas decay constant and α_i and P_Q are the rate constant and partial pressure of the quencher, was measured as a function of the quencher partial pressure for a fixed He partial pressure. In a similar way, the quenching rates for He($3\,^1P$) by Ne, Ar, Kr, and Xe can be measured by monitoring the emission of He($3\,^1P \rightarrow 2\,^1S$) with $\lambda = 5015$ Å. The emissions of He($2\,^1P \rightarrow 1\,^1S$) with $\lambda = 584$ Å, He($3\,^3P \rightarrow 2\,^3S$) with $\lambda = 3889$ Å, and He($3\,^1D \rightarrow 2\,^1P$) with $\lambda = 6678$ Å were also used to measure the quenching rates of these states by foreign gases.

III. RESULTS AND ANALYSIS

We have measured quenching decay rates of several excited states of atomic helium by various foreign gases. The cross sections of these processes were obtained by dividing the experimental rate constants by the thermal rms speed of the reduced mass. Time-resolved data for He($3\,^1P$)-Kr are shown in Fig. 2. The good exponential decay of the data is believed to supply very good accuracy (2%). Including all uncertainties such as pressure reading, flow meter accuracy, etc., the overall accuracy is believed to be within 10% for He($3\,^1P$)-Ne, -Ar, -Kr, -Xe. The decay frequencies against various amounts of foreign gases for these four systems are given in Fig. 3. Numerical values of quenching rates for He($3\,^1P$)-Ne, -Ar, -Kr, -Xe are tabulated in Table I for easy comparison with the results by Kubota *et al.*,[28] and theoretical calculations by Watanabe and Katsuura.[25] The experimental data for He($3\,^3P$) -Ne, -Ar, -Kr, and -Xe are presented in Fig. 4. Numerical values of reaction cross sections and quenching rates are also given in Table I. The quenching cross section of He($2\,^1P$)-Ar was obtained as 142 Å^2 (see Table I), and the experimental results are shown in Fig. 5. The accuracy of the quenching rate for He($2\,^1P$)-Ar is estimated to be within 30%, because of weak emission due

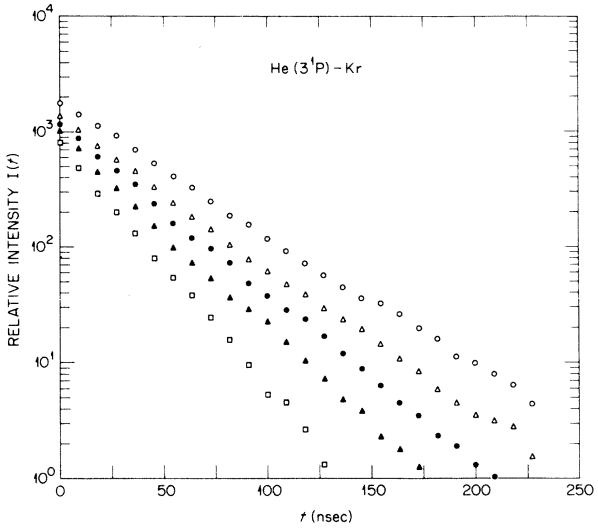

FIG. 2. Experimental data for time-resolved experiments of He($3\,^1P$)-Kr, with He pressure of 2 Torr. ○, △, ●, ▲, and □ represent krypton pressure equal to 0.0, 0.23, 0.57, 0.83, and 1.09 Torr, respectively.

to radiation trapping. The quenching rates of He($3\,^1D$)-Ne are also shown in Fig. 3. Numerical results of this system are also shown in Table I for comparison with the metastable and resonance systems.

The experimental data for time resolved vuv spectra at 601 Å for He($2\,^1S$)-Ar, -Kr, -Xe are pre-

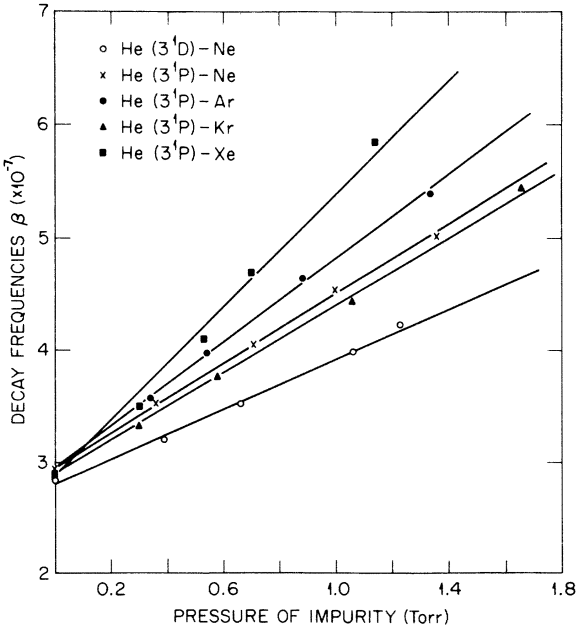

FIG. 3. Decay frequencies versus partial pressure of Ne, Ar, Kr, and Xe, for He($3\,^1P$) quenched by these four gases, and He($3\,^1D$) quenched by Ne. Helium pressure is 2 Torr.

TABLE I. Experimental and calculational values of quenching rates and quenching cross sections of He($2\,^1P$)-Ar, He($3\,^1P$, $3\,^3P$)-Ne, -Ar, -Kr, -Xe, and He($3\,^1D$)-Ne.

	k (10^{10} cm^3 sec^{-1}) [a]	σ_1 (Å^2) [a]	σ_2 (Å^2) [b]	σ_3 (Å^2) [c]	σ_{Ph} (10^{-18} cm^2) [d]	μ_E^2 (a.u.) [e]
He ($2\,^1P$)-Ar	16.6±4.9	142±42		28–84	35–37	4.8–5.7
He ($3\,^1P$)-Ne	4.8±0.5	42±4	$27.6^{+4.5}_{-2.8}$	22.8–23.8	6.4–7.1	0.93–1.03
He ($3\,^1P$)-Ar	5.9±0.6	53±5	$55.6^{+10.6}_{-7.8}$	45.7–46.5	35–37	5.1–5.4
He ($3\,^1P$)-Kr	4.4±0.5	39±4	$49.5^{+8.0}_{-4.6}$	43.9–46.5	29.5–35.5	4.4–5.2
He ($3\,^1P$)-Xe	8.1±0.8	73±7	$73.0^{+12.9}_{-8.8}$	37.7–43.0	21–26	3.0–4.1
He ($3\,^3P$)-Ne	3.9±0.6	32±5	$24.3^{+3.9}_{-2.2}$			
He ($3\,^3P$)-Ar	2.6±0.4	22±3	$25.0^{+6.5}_{-5.7}$			
He ($3\,^3P$)-Kr	1.9±0.3	17±3	$21.5^{+3.4}_{-2.0}$			
He ($3\,^3P$)-Xe	7.5±1.1	67±10	$64.0^{+10.3}_{-6.1}$			
He ($3\,^1D$)-Ne	3.4±0.6	30±5				

[a] Results from this work.
[b] From Refs. 28 and 35 at 600^{+200}_{-100}° K.
[c] Calculational results from the equations in Ref. 25.
[d] From Refs. 36–40.
[e] μ_E^2 is the square of the transition dipole moment.

sented in Fig. 6. Numerical results of this work, beam experimental data, and theoretical calculations are given in Table II.

Some time resolved quenching rates taken on the slow component of the He continuum at 800 Å, emitted by the stabilized He_2, ($A\,^1\Sigma_u^+$), are presented in Fig. 7. These experimental results for argon and krypton quenching are essentially the same as those from He($2\,^1S$) in Fig. 6, within experimental error. This agreement, which is necessary in the model of Ref. 5, supports the suggestion of Ref. 5 that the light emitted by this short-lived molecule is rate limited by the decay of its precursor, He($2\,^1S$).

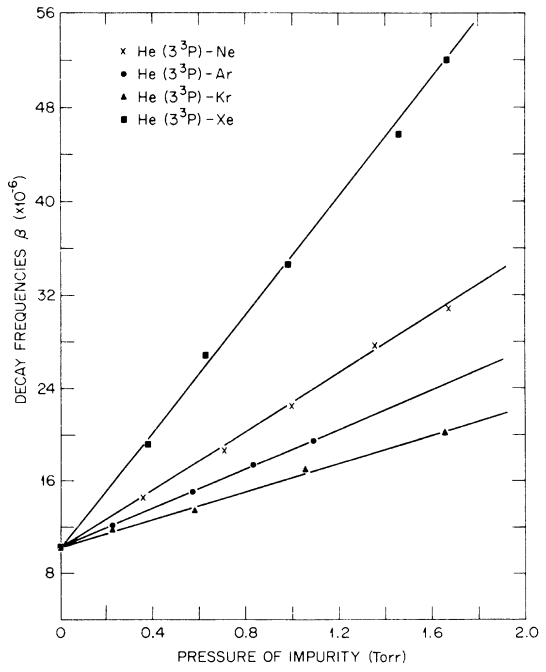

FIG. 4. Decay frequencies of He($3\,^3P$) versus partial pressure of Ne, Ar, Kr, and Xe. Helium pressure is 2 Torr.

IV. DISCUSSION

The quenching cross sections obtained in this work for He($2\,^1S$)-Ar, -Kr, -Xe are in good agreement with the results of beam works by Howard *et al.*[12] and Chen *et al.*,[13] and in disagreement with the discharge work.[9,11] This indicates the fact that we have been able, in the present measurements, to eliminate the nonlinear processes due to recombination and secondary electron emission which were suggested to be responsible for the discrepancy between beam work and some discharge work.[12] This energy-transfer process was calculated by Bell *et al.*[22] by assuming that the bulk of the cross section is determined by a long-range dispersion force. With the orbiting approximation, they reported reaction rates of He($2\,^1S$) quenched by Ar, Kr, and Xe (Table II). The fact that this calculation overestimates the cross section leads us to conclude that this type of interaction force is not justified. This conclusion is also supported by the results of the col-

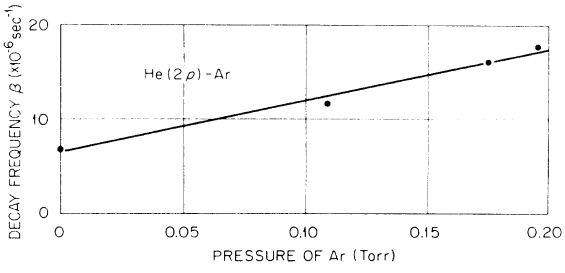

FIG. 5. Decay rate constant for He($2\,^1P$) at 584 Å versus different pressures of Ar. Helium pressure is 90 Torr.

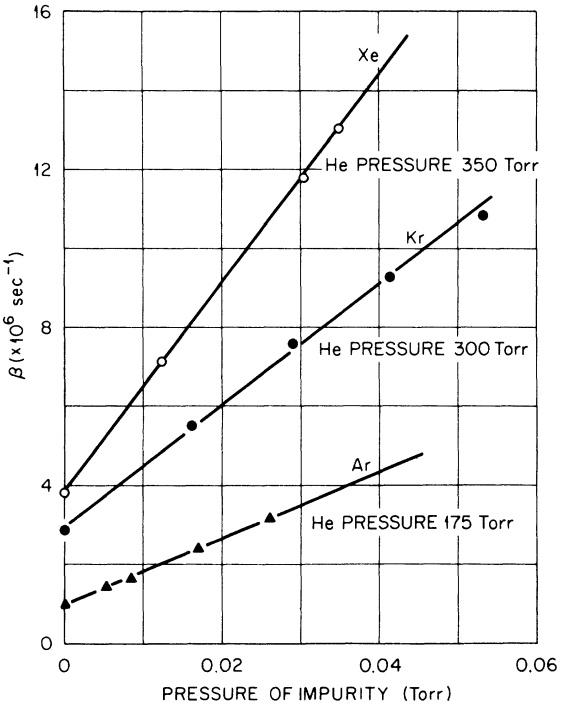

FIG. 6. Decay rate constants at 601 Å versus different pressures of impurity. ▲—He-Ar; ● —He-Kr; ○— He-Xe. Linear least-squares fitting was used to get the straight line.

lisional energy-dependent measurements of beam work[13] and the flowing-afterglow–drift-tube method.[15] These measurements give decay rates that depend very strongly on collisional energy, while the theoretical prediction[22] shows a weak energy dependence. The reason for this strong energy dependence is that the He($2\,^1S$)-Ar, -Kr, -Xe interaction becomes repulsive at internuclear separations around 5 Å, while the imaginary part of the optical potential[13] does not become appreciable until the separation is somewhat smaller. Thus, the latter information leads one to expect an exponential temperature dependence for the rate constant. More time-resolved data at various

TABLE II. Experimental and theoretical calculational values of quenching rates and quenching cross sections of He($2\,^1S$) -Ar, -Kr, -Xe.

	k (cm^3 sec^{-1})	σ_1 (Å^2) [a]	σ_2 (Å^2) [b]	σ_3 (Å^2) [c]
He ($2\,^1S$)-Ar	2.63×10^{-10}	22.5	22.5	85.3
He ($2\,^1S$)-Kr	4.79×10^{-10}	42	42.5	97.7
He ($2\,^1S$)-Xe	8.2×10^{-10}	70	57	114

[a] From this work.
[b] From Refs. 13 and 41.
[c] From calculations by the orbiting approximation in Ref. 22.

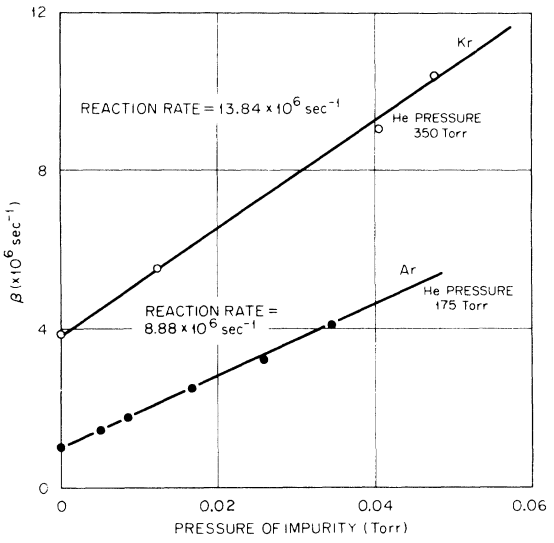

FIG. 7. Decay rate constants at 800 Å (slow continuum in He) versus different pressures of Ar and Kr.

temperatures would help establish detailed interaction potentials and give important information for a theoretical approach.

It is interesting to note that our quenching rates of He($2\,^1S$) by Ar, Kr, Xe, are much larger than the corresponding rates of He($2\,^3S$) obtained by other investigators.[9-13,15] This tends to suggest that the Penning ionization process is more efficient for He($2\,^1S$) than for He($2\,^3S$).[11,13] This conclusion, however, is contradictory to theoretical predictions based on a charge exchange model.[31]

For the resonance states quenching He($3\,^1P$) -Ne, -Ar, -Kr, -Xe and He($2\,^1P$)-Ar, we find quenching cross sections which are much larger than the theoretical predictions.[25] This discrepancy is not due to the collision-induced conversion He($3\,^1P$) to He($3\,^1D$), whose cross section in pure helium is on the order of 10 Å^2 (Refs. 32–34), because over the pressure range of this work, we have detected no significant increase in the intensity of the He($3\,^1D$-$2\,^1P$) emission at 6678 Å. The fact that the theory underestimates the rates leads us to conclude that the Van der Waals force may play an important role in the quenching process; however, detailed interaction potentials may be necessary for the theoretical calculations on these systems.

As in the metastable system, we find discrepancies between the singlet and triplet states of the resonance system. Our results indicate that in the resonance system, the quenching rates of He($3\,^1P$) by Ne, Ar, and Kr are much larger than the corresponding rates of He($3\,^3P$). However, the rates are comparable when Xe is the quenching gas.

From our quenching measurements of He($3\,^1P$; $3\,^3P$) by the various gases and from the results obtained by Kubota *et al.*[35] at 600°K, we find that the quenching rates for He($3\,^1P$; $3\,^3P$)-Ar, -Kr, -Xe have a relatively weak temperature dependence, while those of He($3\,^1P$; $3\,^3P$)-Ne decrease significantly when the temperature increases.

In conclusion, we believe the time-resolved technique provides accurate total rates for energy transfer. Results of these studies, particularly when generalized through energy pathways models, can supply important information not only for theoretical interest but also for laser applications.

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