Time-Dependent Studies of Vacuum-Ultraviolet Emissions from Helium*

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Proton excitation was employed to obtain new information on the vacuum-ultraviolet (vuv) emissions from helium gas. Time-dependent studies of the 584-Å resonance line and the vuv continuum (600-950 Å) have been made as a function of pressure. The decay rate for 584-Å resonance photons shows a type of pressure dependence which indicates that the 2^1P atomic state is destroyed much more rapidly by collisions than by radiation to the 2^1S metastable state. Most of the vuv continuum decays with two time components (fast and slow). The number of ions and the population of the lowest-ten excited states resulting when an energetic (4-MeV) proton loses a fraction of its energy in helium, and when the secondary electrons completely degrade in energy, have been calculated. The theoretical studies indicate that about 30% of the energy lost by a single proton goes into atomic excitation, where about one-half of these excited states are 2^1P states. These new results are combined with previous information to propose an energy pathways model for helium. We suggest that the 2^1P state is primarily destroyed by collisions to the D and B molecular states which are then the source of the fast vuv radiation (640–950 Å) and the precursor of slow radiation, respectively. In our model the metastable B molecular state stores the energy which is utilized in producing additional ionization (Jesse effects) when impurities are added to helium, in contrast with previous interpretations which assumed that the energy is stored in atomic metastable states.

I. INTRODUCTION

Studies of the interaction of charged particles with the noble gases, when pursued with the objective of understanding such diverse phenomena as the Jesse effect[1,2] and the vacuum-ultraviolet (vuv) continuous-emission spectra, are both intricate and fascinating. By the Jesse effect we mean the large increase in ionization yield that occurs when certain impurities are added to a noble gas; e.g., the ionization of helium owing to charged particles is increased 28% by the addition of just 0.02% argon.[3] The extensive literature (see, e.g., Refs. 4–19) on noble-gas vuv emission of atomic lines and continuous spectra for various modes of excitation (e.g., gas discharge, microwave, and charged particle) does not explain the detailed mechanisms for the continuous emission. Likewise, there are unresolved questions concerning the type of excited states which produce the Jesse effect.[1,19] Because certain excited atomic states could be the origin of both the vuv continuous emission and the Jesse effect, we study these topics in close relationship to each other.[20]

In search of unifying models of the energy pathways following the interaction of radiation with matter, a systematic study was initiated wherein fast monoenergetic charged particles are used to irradiate the noble gases. The quantities measured are (i) the average energy expended by the radiation per ion pair it produces (W value)[3]; (ii) the intensity of the vuv light as a function of wavelength for the same noble gases[13,14,17,18]; (iii) the fraction of energy lost by the charged particles that goes into vuv light emission $(d\epsilon/dx)$[14,20]; (iv) the formation and decay times of the emission spectra at different wavelengths[19]; (v) Jesse effects due to the addition of impurities[3]; and (vi) the quenching of the light with the addition of the same impurities.[21] All of these experiments are done over a wide range of pressures (under similar conditions) and under conditions where the charged particles lose only a small fraction of their energy in the gas.

Emission studies done with monoenergetic-proton excitation are reproducible and they can be done over a wider pressure range than in discharge experiments. The well-defined initial conditions of monoenergetic-proton excitation invite theoretical treatment and permit simple estimations, e.g., with the optical approximation.[22]

In the present work the initial steps of a proton's action in helium (ionization and excitation by protons and secondary electrons) are treated theoretically. We also report time-dependent studies of the vuv emission stimulated by proton excitation of helium. These new inputs are combined with previous measurements of proton-induced emission and ionization to suggest a model for the vuv emission and the Jesse effect in helium.

II. CALCULATIONS OF PROTON EXCITATION AND IONIZATION IN HELIUM

Some insight into the initial stages of the interaction of protons (1–4 MeV) with helium can be obtained using theoretical techniques. Although this type of calculation has been made for electrons[23–26] and alpha particles[27] in helium, there are no published results for directly interpreting the experi-

ments involving proton irradiation.

Proton excitation[28] and ionization[29] cross sections have been obtained by using the Born approximations. Cross sections $\sigma(e,E)$ for 4-MeV protons were obtained by using the estimate

$$\sigma(e,E)=[Y(e)\ln E+Z(e)]/E. \quad (1)$$

The parameters $Y(e)$ and $Z(e)$ were determined at each secondary-electron energy e by using the available cross sections[30] for protons of energy $E=1$ and 2 MeV. Cross sections for secondary electron energies above 326.52 eV were reckoned by using the classical binary-encounter collision model.[31]

The amount of ionization and the population of the lowest-ten excited states produced by the spectrum of secondary electrons were determined by using Alkhazov's[25] results and treating the electrons at each energy individually. Alkhazov's publication was used because he calculated the energy degradation for electrons of many energies, and he included the individual populations of many excited states as well as the number of ions produced. Integrations of Alkhazov's data for the secondary-electron spectra were done by the trapezoid technique. Alkhazov's populations were assumed to be linear with electron energy for energies greater than 172 eV. The proton's energy was assumed to be constant as it passed through a 1-cm path in 400 Torr of helium. Further details of the calculation can be found in Ref. 32.

Uncertainties in the populations of specific excited states reflect some inaccuracies in Alkhazov's work; 20–30% in the case of S, D, and ^3P levels. He reports a 3–5% error in the ionization cross sections used. One would expect that errors in the proton cross sections are minor compared to those of the secondary-electron degradation.

The results of the first stages of a proton's interaction in helium are displayed in Fig. 1 for 4-MeV protons. These results are in rough agreement with three fundamental experiments that were mentioned in Sec. I: the W value $d\epsilon/dx$ and the magnitude of the Jesse effect in helium. It is shown (Table I) that the relative distribution of excited states and ions does not depend strongly on the proton energy. Calculations were made at 1 MeV and then compared to the 4-MeV results by multiplying the 1-MeV calculations by the ratio of the proton stopping power at 4 MeV to the stopping power at 1 MeV.

The W value cannot be calculated simply by dividing the total ion pairs tabulated in Fig. 1 by the energy lost because account must be made for molecular ions,[33]

$$\mathrm{He}^* + \mathrm{He} \rightarrow \mathrm{He}_2^+ + e^-. \quad (2)$$

Although all highly excited states of helium (states with principal quantum number greater than 3) have sufficient energy to form ions,[34] there is evidence that collisional deexcitation competes with the molecular-ion process.[35] The measured W value (45.5 eV/ion pair)[3] lies between the W value calculated when the molecular-ion process is taken to be 100% efficient (42.3 eV/ion pair) and when it is neglected (46.4 eV/ion pair).

Stewart *et al.*[14] determined that 2200 eV of vuv radiation ($d\epsilon/dx$) results when a 4-MeV proton passes through 1 cm of helium at 400 Torr. The theoretical estimate of 2770 eV for the magnitude of the atomic-excitation energy at first seems too high. However, the measured vuv emission is continuous, indicating that some of the atomic-excitation energy is converted to kinetic energy in the emission process. Other atomic-excitation energy goes to form molecular ions of helium. In addition, the small amount of radiation at optical wavelengths was, of course, not included in the vuv measurement.

If the energy source for the Jesse effect is atomic states, then the Jesse effect is saturated when

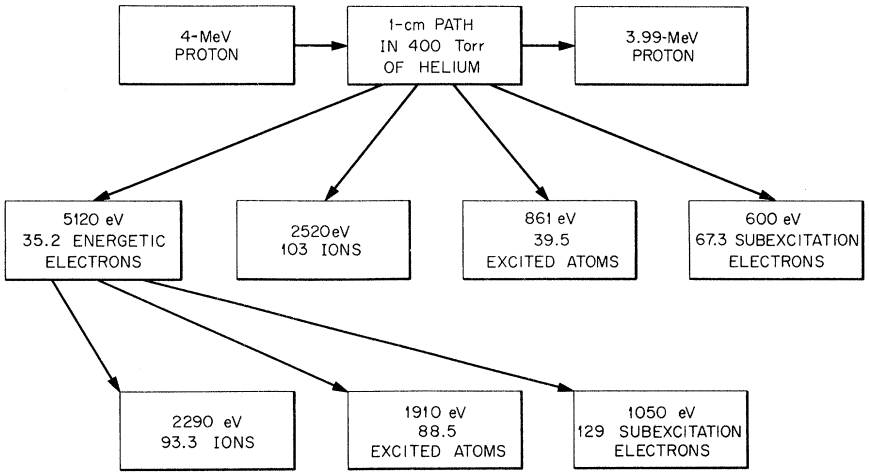

FIG. 1. Calculated energy degradation when a 4-MeV proton loses a fraction of its energy in helium. The energies given are the portions of the 9101 eV lost by the proton that appear in the species indicated. The numbers of those species produced are also indicated.

TABLE I. Average populations resulting when one proton has a 1-cm path in 400 Torr of helium.

Products	4-MeV proton Primary proton	4-MeV proton Secondary electrons	1-MeV proton (scaled)[a] Primary proton	1-MeV proton (scaled)[a] Secondary electrons
$2\,^1S$	1.40	8.82	1.88	8.91
$3\,^1S$	0.31	1.71	0.42	1.73
$2\,^1P$	25.3	27.6	24.0	25.6
$3\,^1P$	6.24	6.32	5.94	5.83
$3\,^1D$	0.07	1.03	0.10	1.03
$2\,^3S$		16.0		16.3
$3\,^3S$		1.56		1.58
$2\,^3P$		8.67		8.87
$3\,^3P$		1.77		1.85
$3\,^3D$		1.85		1.67
Other atomic levels	6.08	13.2	6.01	12.8
Ions	103	93.3	108	85.1

[a]By the ratio of the stopping power at 4 MeV to the stopping power at 1 MeV.

every available excited atom has given its energy to ionize an impurity atom or molecule. The total number of ions resulting when, e.g., argon is added to helium is the number of helium atomic ions plus the helium molecular ions plus the ions produced in argon by the Jesse effect, and this sum is approximately the number of helium ions plus the number of excited helium atoms. The role of sub-excitation electrons with energies greater than the ionization potential of the impurity has been neglected. The W value calculated is 28.4 eV/ion pair. Parks[3] obtained 29.5 eV/ion pair for a mixture of 1% argon in helium. The reason for disagreement between the two values could be that there are intermediate steps in the Jesse-effect process and that the available energy is not always sufficient to ionize the impurity. Such intermediate steps are suggested in a later section.

Of particular importance to energy pathways studies is that 30% of the energy lost by the proton goes into excited atoms and of these excited atoms about half are in the 2^1P state.

III. TIME-DEPENDENT STUDIES OF WAVELENGTH-RESOLVED vuv EMISSIONS

The experiment is represented schematically in Fig. 2. A pulsed beam of 2-MeV protons passes a time-pickoff unit and some protons are Rutherford scattered into a parallel-plate ionization cell by a gold foil.[3] Moving the foil out of the beam allows the protons to enter a cylindrical stainless-steel emission cell which also serves as a Faraday cup. Leaving the gold foil in the beam is not desirable when making emission studies because of beam scattering. Photons are dispersed using a differentially pumped monochromator[14] and are detected with a channel-electron-multiplier photon detector. Further details of the apparatus can be found in Ref. 32. Time-dependent spectra were observed by repeatedly measuring the time between a burst of protons and the emission of a spectrally ana-

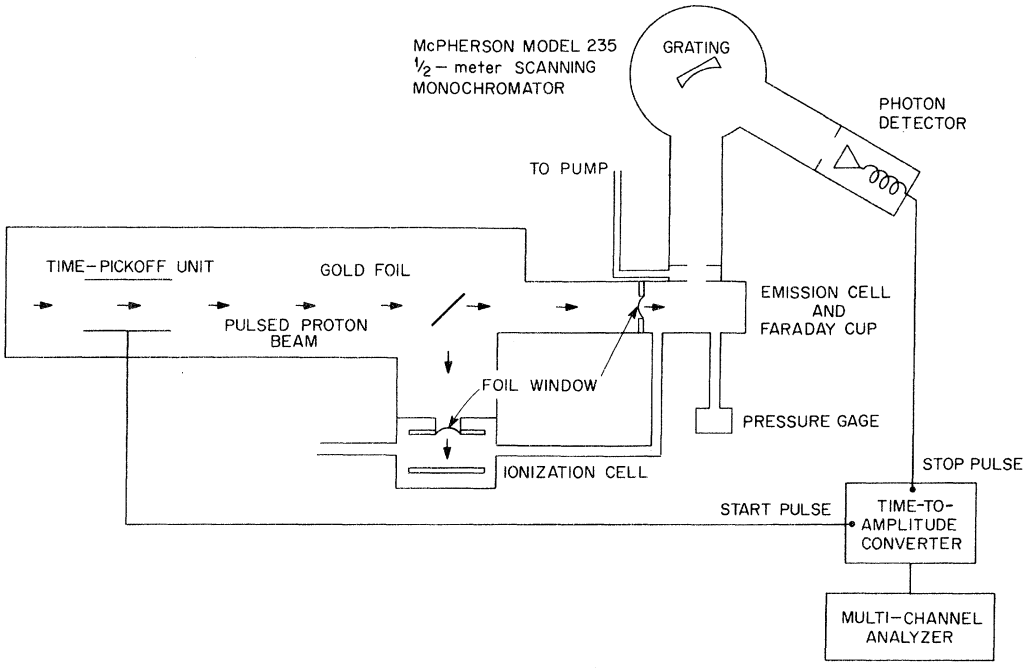

FIG. 2. Schematic representation of the apparatus for measuring vuv emission and ionization produced by proton excitation of noble gases.

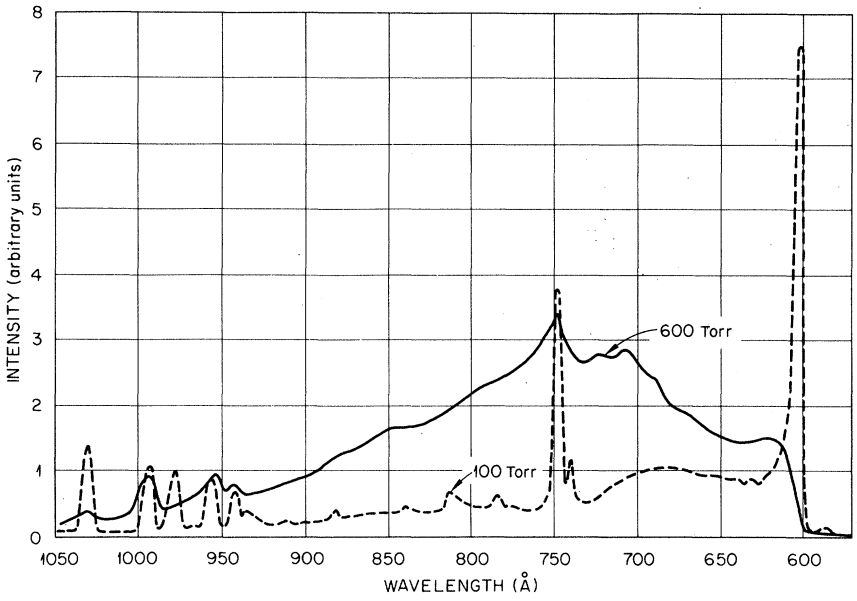

FIG. 3. Emission spectra of proton-excited helium at 100 and 600 Torr.

lyzed photon. The time resolution of the apparatus was about 0.1 μsec.

W-value experiments are a convenient way to verify the purity of helium gas[14] and W values were measured almost concurrently with the time-dependent studies. A good grade of helium (99.9999% purity) was used in this work and the W values were in the range of 42–44 eV/ion pair except where otherwise noted.

The time-unresolved spectra (Fig. 3) show the 601-Å peak with its small adjoining continuum, the 675-Å continuum extending from about 650 to 750 Å, the 800-Å continuum extending from about 750 to 1000 Å, and other atomic lines. Possible sources of the atomic lines have been listed previously. These spectra are nearly identical to those observed by Stewart *et al.*[13] Time-dependent measurements were made throughout the vuv region at pressures from 5 to 1000 Torr.

Following excitation the intensity of the 584-Å line (2^1P to 1^1S transition) increases rapidly (within the time resolution) to a maximum and then decreases exponentially (Fig. 4). The decay rate u_1 was determined by fitting the data to

$$I(t) = A_1 e^{(-u_1 t)} + A_0, \tag{3}$$

where $I(t)$ is the intensity of emitted light at time t and A_1 and A_0 are constants. The decay rate u_1 increases with pressure from 5 to 150 Torr (Table II and Fig. 5). Data were taken within a limited pressure range (5–150 Torr) because of intensity and time-resolution restrictions.

Time-dependent spectra of the 601-Å peak show a two-component exponential decay (Fig. 6). The

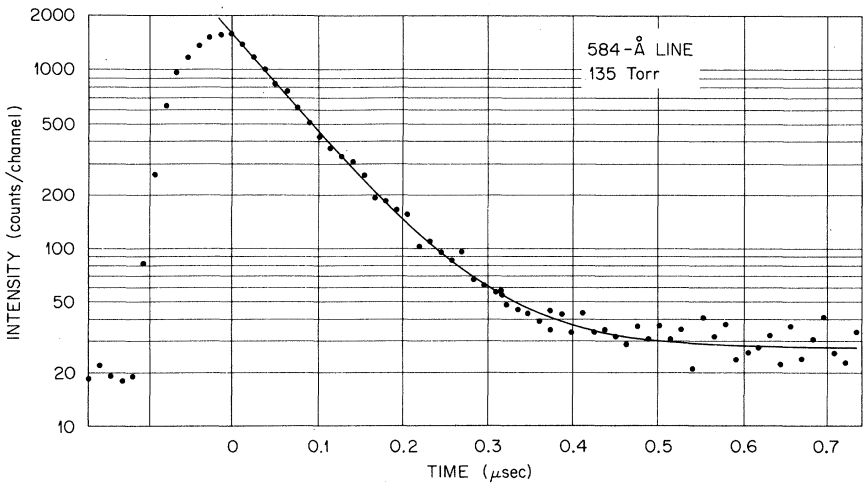

FIG. 4. Time dependence of the intensity of the 584-Å line ($2^1P \rightarrow 1^1S$) in helium at 135 Torr.

TABLE II. Calculated parameters for time dependence of the 584-Å line.

Run No.	Pressure (Torr)	u_1 (10^6 sec^{-1})	A_1	A_0
157	5.4	3.02	973	−14
56	10	3.49	2690	4
47	24.5	4.29	3095	11
45	50	5.87	1699	6
153	71.2	7.28	1894	10
158	86.3	9.00	2618	21
154	102	9.73	2198	23
155	121	11.4	1772	26
156	135	12.8	1589	28
55B	151	13.8	1539	58

data were fitted to

$$I(t)=A_2e^{-u_2t}+A_3e^{-u_3t}, \quad (4)$$

where u_2 is the decay rate of the main component and u_3, A_2, and A_3 are other constants. The decay rate at the 601-Å peak is proportional to pressure squared from 200 to 800 Torr (Fig. 7 and Table III).

The 675- and 800-Å continua have almost identical time dependence (Fig. 8). Following excitation, the intensity builds up to a maximum within the resolution time, decays to one-half intensity very rapidly (0.3 μsec, hereafter called the fast component), and then both continua complete their decay at a rate which is indistinguishable from that of the 601-Å peak (slow component). The results were analyzed (Fig. 7, Table IV) by omitting the fast component of the decay curve and then implementing the same analysis used for the 601-Å peak [Eq. (4)] for the slow component. The fast component is more pronounced at wavelengths above 630 Å (Fig. 9). Moreover, the fast-component rate is pressure dependent (Fig. 10). However, the ratio of the fast-component to slow-component intensities is constant with pressure and with wavelength[32] from 660 to 950 Å.

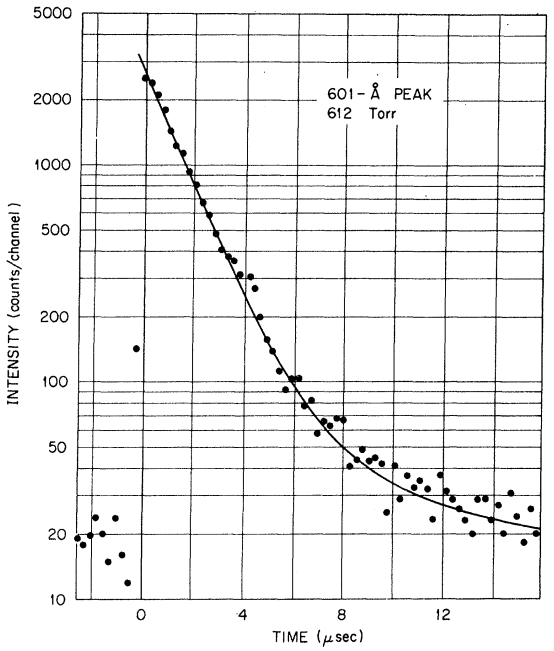

FIG. 6. Time dependence of the 601-Å peak in helium at 612 Torr.

IV. ENERGY PATHWAYS

An energy pathways model in helium should be consistent with vuv emission intensity studies, Jesse-effect measurements, time-dependent vuv-

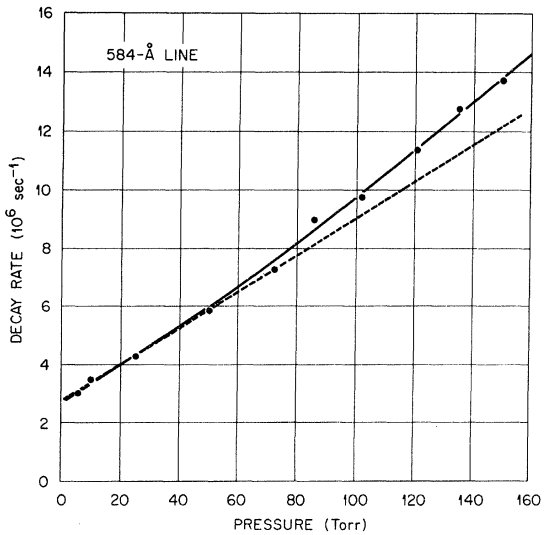

FIG. 5. Pressure dependence of the 584-Å decay rate u_1. The dotted curve is a straight line through the low-pressure data points.

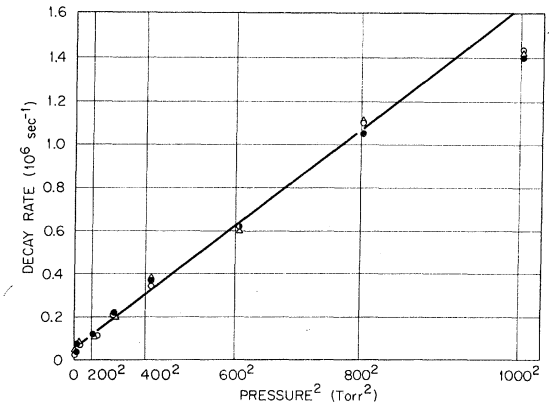

FIG. 7. Pressure dependence of the decay rate u_2 of the main component of the continuum. Open circles, 601-Å peak; closed circles, 675 Å; closed triangles, 825 Å.

emission experiments, theoretical treatment of the first stages of radiation action, and He_2 potential-surface data. In the model suggested (Fig. 11), energy from the proton and secondary electrons excite helium atoms to the 2^1P state. This state is depleted by three-body collisions yielding helium molecules in both the D and B excited states (Fig. 12). The fast component in the vuv continuum results when the D state radiates to the ground state. The rate-determining step for the slow component of the continuum is a three-body collision which converts the metastable B state to the radiating A state. The metastable B molecular state stores energy which is utilized in producing Jesse effects when impurities are added to helium. These remarks will be amplified in what follows.

A. Model for vuv Emission

Protons and the electrons they produce excite low-lying atomic states and about one-half of these are 2^1P states (Table I). At very low pressures the 2^1P excitation energy is depleted mainly by emission of 584-Å photons (2^1P to 1^1S) at a rate[36] of 1.8×10^9 sec^{-1}. However, at the intermediate pressures (10^{-4} Torr and above) the 584-Å photons are absorbed and reemitted many times by neighboring helium atoms (trapping of resonance photons) so that the effective rate[37] of escape β of these photons from our apparatus is about 10^6 sec^{-1}. Under these conditions, the much slower emission process (2^1P to 2^1S) occurring at a rate of 1.9×10^6 sec^{-1} becomes important, so that one expects

TABLE III. Parameters for the time dependence of the 601-Å peak.

Run No.	Pressure (Torr)	u_2 (10^6 sec^{-1})	u_3 (10^6 sec^{-1})	A_2	A_3
55*A*	51	0.039	0.011	815	939
140	102	0.080	0.033	1697	3650
34[a]	212	0.110	0.020	14619	300
175[b]	202	0.121	0.036	8586	145
123[c]	206	0.113	0.025	12934	277
186	301	0.204	0.078	10751	409
31	416	0.341	0.032	2097	66
37	612	0.616	0.055	2681	51
179	803	1.10	0	1311	22
74	1002	1.43	0.115	2060	48

[a] $W = 43.8$ eV/ion pair. [c] $W = 42.7$ eV/ion pair.
[b] $W = 40.0$ eV/ion pair.

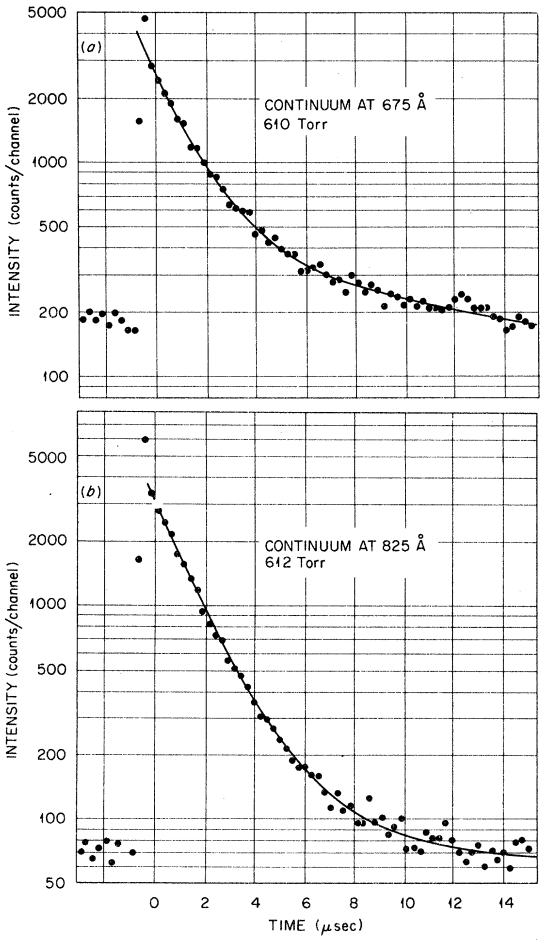

FIG. 8. Time dependence at 675 and 825 Å in helium at 610 Torr.

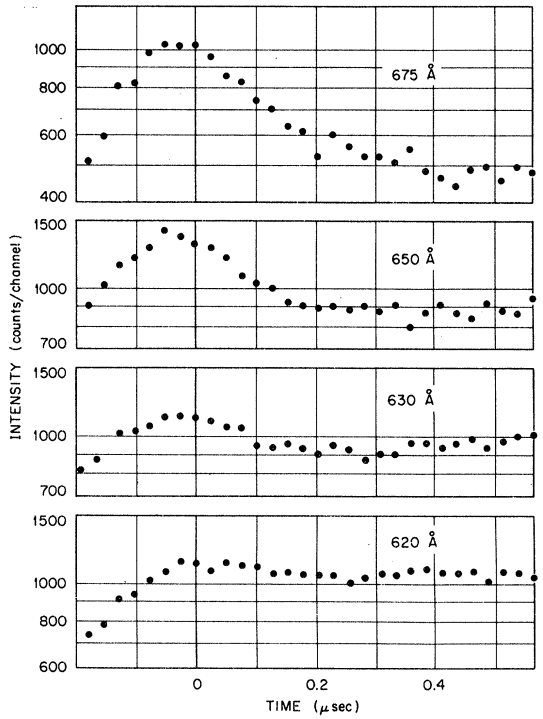

FIG. 9. Time dependence of the fast component at several wavelengths, all at a helium pressure of 102 Torr.

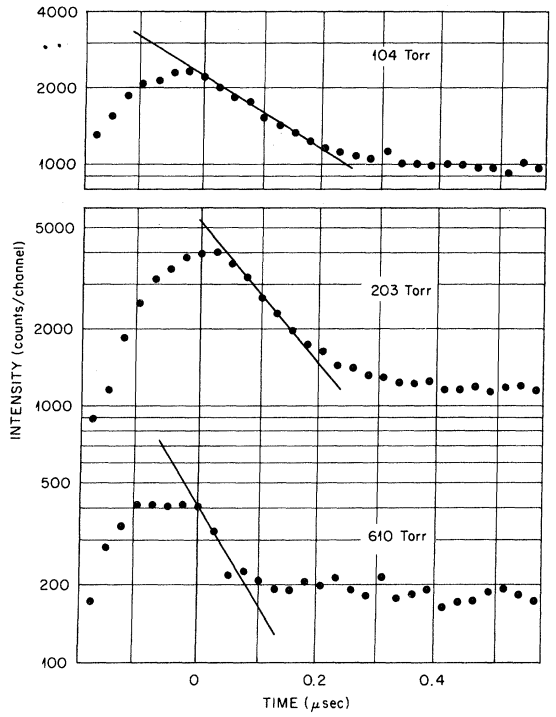

FIG. 10. Time dependence of the fast component at 675 Å for several helium pressures.

TABLE IV. Parameters for the time dependence at 675 and 825 Å.

Run No.	Pressure (Torr)	u_2 (10^6 sec^{-1})	u_3 (10^6 sec^{-1})	A_2	A_3
		675 Å			
57[a]	50	0.039	0.011	576	629
27C	100	0.072	0.028	2192	2576
32[b]	209	0.107	0.020	4456	648
128[c]	207	0.110	0.042	837	256
176[d]	202	0.120	0.033	2061	56
185	300	0.219	0.090	2569	614
30	416	0.369	0.031	832	308
35	610	0.617	0.050	2064	368
180	802	1.05	0.119	838	123
231	1006	1.40	0.098	628	20
		825 Å			
59[a]	50	0.035	0.009	442	328
28	100	0.081	0.028	1465	1779
33[b]	209	0.107	0.015	6164	397
133[e]	208	0.111	0.019	2343	113
177A[d]	202	0.114	0.036	1894	36
188	303	0.198	0.030	3406	94
29	416	0.379	0.030	861	202
36	612	0.596	0.035	2703	112
181	803	1.11	0.076	1224	81
85[f]	1003	1.42	0.051	2442	96

[a] $W = 40.9$ eV/ion pair.
[b] $W = 43.8$ eV/ion pair.
[c] $W = 42.7$ eV/ion pair.
[d] $W = 40.0$ eV/ion pair.
[e] $W = 42.7$ eV/ion pair; 800 Å.
[f] 800 Å.

the total rate of decay of the 2^1P state to be about 1.9×10^6 sec^{-1} plus 1×10^6 sec^{-1}, or about 3×10^6 sec^{-1}. This value is close to the low-pressure intercept of u_1 in Fig. 5. There is also collisional deexcitation of 2^1P as evidenced by the increase in the 2^1P destruction rate with pressure (Fig. 5). There is evidence of both a linear and quadratic term in the pressure dependence of the 2^1P de-

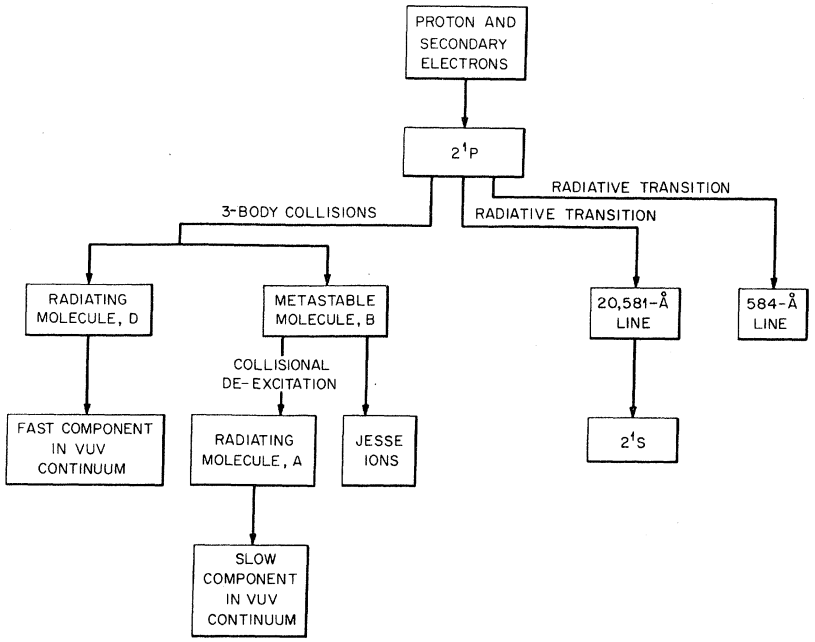

FIG. 11. Energy pathways model describing the fate of excited states in helium mixtures.

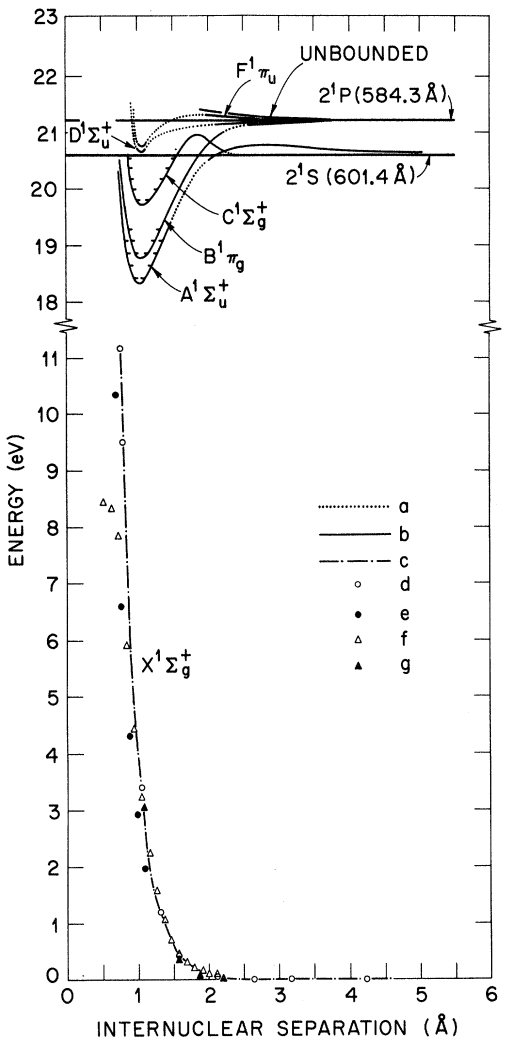

FIG. 12. Potential energy curves for selected states of He_2. (a) Hypothetical curves. (b) M. L. Ginter and R. Battino, J. Chem. Phys. 52, 4469 (1970); M. L. Ginter (private communication); C. R. Scott, E. M. Greenawalt, J. C. Browne, and F. A. Matsen, J. Chem. Phys. 47, 4862 (1967); H. C. Schweinler (unpublished data). (c) and (d) D. J. Klein, C. E. Rodriguez, J. C. Browne, and F. A. Matsen, J. Chem. Phys. 47, 4862 (1967). (e) J. E. Jordan and I. Amdur, J. Chem. Phys. 46, 165 (1967). (f) P. Rosen, J. Chem. Phys. 18, 1182 (1950). (g) N. Moore, J. Chem. Phys. 33, 471 (1960). A recent paper [S. L. Guberman and W. A. Goddard, III, Chem. Phys. Letters 14, 460 (1972)] suggests that the heights of the bumps in the A and C states are 0.06 and 0.22 eV, respectively.

struction rate u_1. That is,

$$u_1 = A + BP + CP^2. \tag{5}$$

The P^2 dependence of u_1 is due to depletion of the $2\,^1P$ state by collisions with two ground-state helium atoms forming an excited molecule:

$$\mathrm{He}(2\,^1P) + 2\,\mathrm{He}\,(1\,^1S) \rightarrow \mathrm{He}_2\,(B \text{ or } D) + \mathrm{He}\,(1\,^1S) + T_{\mathrm{KE}}. \tag{6}$$

(T_{KE} is the kinetic energy released.) The D and B molecular states (Fig. 12), being attractive without potential bumps, can be readily formed by this process.

The allowed D to X transition may result in the vuv continuum's fast component in the process

$$\mathrm{He}_2(D) \rightarrow \mathrm{He}_2\,(X) + \text{vuv light}. \tag{7}$$

The observed spectrum (640–950 Å) of the fast component of the vuv emission is consistent with the energy separation of the D and X potential surfaces.

The slow component in the vuv continuum appears to depend on the collisional deexcitation of the metastable B state to the radiating A state, i.e.,

$$\mathrm{He}_2\,(B) + 2\,\mathrm{He}\,(1\,^1S) \rightarrow \mathrm{He}_2\,(A) + 2\,\mathrm{He}\,(1\,^1S) + T_{\mathrm{KE}}. \tag{8}$$

The final step in the slow-component emission is then

$$\mathrm{He}_2\,(A) \rightarrow \mathrm{He}_2\,(X) + \text{vuv light}. \tag{9}$$

The evidence that the collisional deexcitation of He_2 (B) is a three-body process, is the pressure-squared dependence of the continuum's slow-component decay rate u_2 (Fig. 7). We observed experimentally that the slow component of the vuv emission spectrum is slightly wider than the spectrum of the fast component. The slow component extends to near 601 Å, while the fast component stops near 630 Å. These facts, again, are consistent with the energy spacings shown in Fig. 12 for the D, A, and X states.

It has been common practice, ourselves[13] included, to assume that the metastable $2\,^1S$ state is a substantial energy source for the vuv continuum. However, the theoretical work shows that protons (and secondary electrons) excite the $2\,^1P$ state preferentially. Furthermore, the time-dependent measurements of the 584-Å line (Fig. 5) reveal the very surprising fact that at pressure above 100 Torr the $2\,^1P$ state is destroyed much more rapidly by collisions than by the allowed transition to the $2\,^1S$ state.

In contrast to early interpretations,[5,9,13] the D to X radiation is not limited to the 675-Å region but also includes radiation in the 800-Å region. The A to X transition yields the very wide vuv continuum ranging from 601 Å to at least 950 Å. In short, there are indeed two continua but they are distinguishable on the basis of time rather than wavelength.

The above interpretation does not account for the linear pressure term in the 584-Å decay rate. It is possible that the linear pressure term is Franck–Condon emission, which is very near the 584-Å line. It is also possible that the linear pressure term is unreal, i.e., the 584-Å decay is merely a combination of a pressure-dependent β and a pressure-squared term.

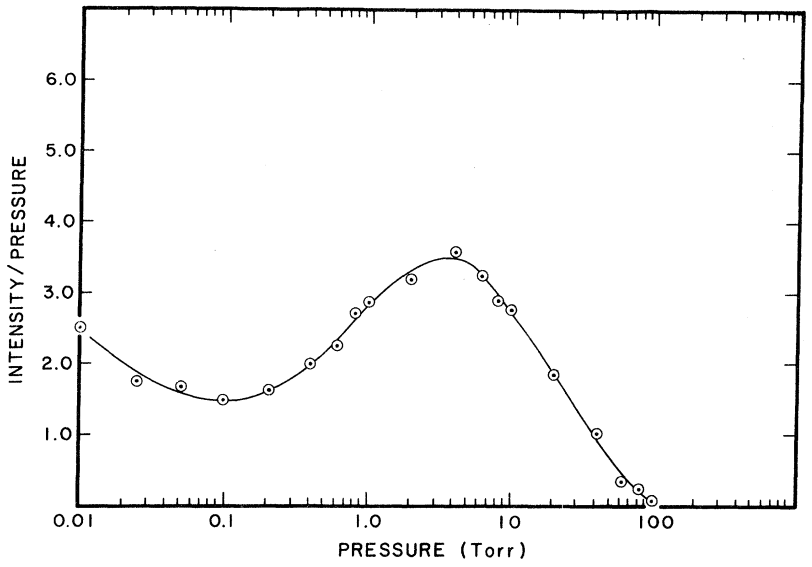

FIG. 13. Intensity divided by pressure plotted as a function of pressure for the He 584-Å resonance line.

Stewart's data[13] for the pressure dependence of the vuv-emission intensity, produced when protons excite helium, will be commented upon using the present model. The 548-Å data (Fig. 13) in the range of pressure (5–100 Torr), where the intensity per unit of pressure is declining, is consistent with the idea that collisional deexcitation competes with 584-Å radiation for the $2\,^1P$ excitation energy. The intensity of the vuv continuum (Fig. 14) at higher wavelengths increases with pressure at the expense of radiation at shorter wavelengths. This variation may be due in part to collisional deexcitation to lower vibrational levels within the D, B, and A molecular states, but may be influenced as well by radiation from higher molecular states.

The small very slow secondary component [last term in Eq. (4)] of the vuv continuum could be due to the slow collisional depletion of He $(2\,^1S)$ and He $(2\,^3S)$ atoms.[38] Finally, we comment on the rate of decay of the main continua measured at 1000 Torr (Fig. 7). The deviation from the pressure-squared line could indicate that the radiation rate of the A state is comparable to the rate of collisional deexcitation when the pressure is 1000 Torr, i.e., comparable to 2×10^6 sec^{-1}.

B. Model for the Jesse Effect

We suggest that the metastable $He_2(B)$ molecule is the energy source for the Jesse effect in helium. The reasons for this suggestion are that the vuv continua and the Jesse effect have a common energy source,[20] the major portion of the vuv energy (the slow component) is available from the $He_2(B)$ molecules, and the process competing with the Jesse effect [collisional deexcitation to the He_2 (A) state] has a slow rate. Using argon as an example, the competing processes are

$$He_2\,(B) + Ar \rightarrow He_2\,(X) + Ar^+ + e^- + T_{KE}, \tag{10}$$

$$He_2\,(B) + 2\,He\,(1\,^1S) \rightarrow He_2\,(A) + 2\,He\,(1\,^1S) + T_{KE}. \tag{11}$$

This model conflicts with previous models[1] where it was said that the Jesse-effect energy comes from atomic-metastable-excitation energy.

A rate for the Jesse effect can be derived by

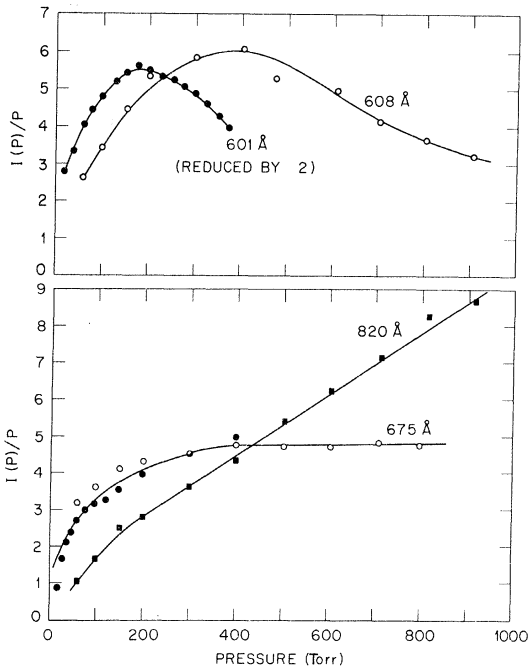

FIG. 14. Intensity divided by pressure plotted as a function of pressure for the vuv-emission continuum of helium.

using Parks's ionization data[3] in context with the time-dependent measurements. The number of ion pairs in the argon-helium mixture N is given by

$$N = N_0 + (kP_{Ar}N^*)/(kP_{Ar} + \lambda), \tag{12}$$

where N_0 is the number of ion pairs in the pure gas, kP_{Ar} is the Jesse-effect rate, k is a proportionality constant to be determined, P_{Ar} is the partial pressure of argon, λ is the deexcitation rate of the metastable molecules, and N^* is the number of metastable $He_2(B)$ molecules. We divide by N_0 and use the equality

$$N/N_0 = W_0/W, \tag{13}$$

where W_0 is the W value of pure helium (45.5 eV/ion pair)[3] and W is the W value of the mixture. These substitutions yield

$$W_0/W = 1 + (kP_{Ar}N^*/N_0)/(kP_{Ar} + \lambda). \tag{14}$$

When a sufficient amount of argon (about 1% of the volume) is added to helium, the Jesse effect dominates so that W drops to an argon-saturated value W_s (29.5 eV/ion pair)[3]

$$W_0/W_s = 1 + N^*/N_0. \tag{15}$$

Hence the quantity N^*/N_0 is obtained and the equation for k is expressed in terms of experimentally determined parameters

$$\frac{W_0}{W} = 1 + kP_{Ar}\left(\frac{W_0/W_s - 1}{kP_{Ar} + \lambda}\right). \tag{16}$$

From Fig. 7, $\lambda = 1.6P^2$, where λ is in sec^{-1} and P is in Torr. For various values of pressure in the range 200–800 Torr, k is about 1.0×10^7 $Torr^{-1}$ sec^{-1} (Table V), corresponding to a rate constant of 2.7×10^{-10} cm^3 sec^{-1}. In comparison, the magnitude of the calculated rate constant for ionization of argon upon collision with helium atoms in the 2^1P excited state is about 9.5×10^{-10} cm^3 sec^{-1},[39] and the measured deexcitation rates of the metastable states are 2^1S, 2.2×10^{-10} cm^3 sec^{-1} and 2^3S, 0.74×10^{-10} cm^3 sec^{-1}.[40]

The magnitude of the Jesse effect varies with the type of gas that is added to helium[41] and this small deviation has been previously attributed to subexcitation electrons.[42] However, the reason for this variation may be that there is a spectrum of energy [the difference between the $He_2(B)$ and $He_2(X)$ surfaces] available for Jesse effects. Jesse's data[41] for helium mixtures show that adding xenon to saturation produces about 20% more additional ion pairs than when argon is added to saturation. This difference is compatible with the available energy for ionizing these atoms as reflected in the vuv spectra.[13]

TABLE V. Jesse-effect rate for argon in helium.

Total pressure (Torr)	W(eV/ion pair)	k (10^7 $Torr^{-1}$ sec^{-1})
0.002 49% argon in helium		
59.72	34.43	0.56
80.05	35.89	0.50
108.64	36.19	0.63
204.39	37.64	0.82
305.46	38.77	0.92
411.86	39.53	1.02
502.00	39.92	1.12
602.64	40.72	1.07
705.49	40.84	1.21
812.55	41.61	1.09
910.64	41.91	1.10
1011.68	42.57	0.94
0.0985% argon in helium		
104.69	29.72	0.79
202.41	29.96	0.72
302.51	30.09	0.83
410.44	30.33	0.79
506.15	30.37	0.93
607.72	30.56	0.90
704.40	30.69	0.92
812.70	30.77	0.99
902.36	30.86	1.02
1008.90	31.04	1.00

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Density Expansion of the Memory Operator in Pressure-Broadening Theory

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The motion of a radiating atom immersed in a gas of other atoms, the bath, may be described by means of a nonunitary time-evolution operator $U(t) = (\mathrm{Tr}_B\rho)^{-1}\,\mathrm{Tr}_B\rho e^{itH^\times}$ acting in its Liouville space (Tr_B is the trace over bath variables, ρ is the density matrix, and $H^\times$ is the quantum-mechanical Liouvillian). In a previous paper, $U(t)$ was written in the form $U(t) = \exp_-[i\int_0^t dt'\,L_1(t')]$ ($\exp_-$ denotes a time-ordered exponential), and the time-dependent *effective Liouvillian* $L_1(t)$ was expanded in powers of a "reduced density," or *activity*. In this paper the Fourier transform $U(\omega) = \int_0^\infty dt\,e^{-i\omega t}U(t)$ is written in the form $iU(\omega) = [\omega - L_2(\omega)]^{-1}$, and the frequency-dependent *effective Liouvillian* $L_2(\omega)$, or "memory operator," is expanded in powers of the reduced density. It is argued that in treating $L_2(\omega)$ to first order in the reduced density, one effectively allows the radiator to interact with only one perturber at a time, thus neglecting all multiple-collision effects. This is in contrast to performing the same-order approximation on $L_1(t)$, which is equivalent to treating different perturbers as uncorrelated, but still allows for multiple-collision effects. By adding the terms of higher order in the expansion of $L_2(\omega)$, one allows the radiator to interact simultaneously with two, three,... perturbers.

I. NOTATION

The time variable τ and the frequency ω will be considered conjugate variables in the sense that for any function $f(\tau)$:

$$f(\omega) \equiv \int_{-\infty}^{\infty} d\tau\, e^{-i\omega\tau} f(\tau) \equiv \mathfrak{F}\{f(\tau)\}\,,$$

$$f(\tau) \equiv (2\pi)^{-1} \int_{-\infty}^{\infty} d\omega\, e^{i\omega\tau} f(\omega) \equiv \mathfrak{F}^\dagger\{f(\omega)\}\,,$$

where $\mathfrak{F}$ means Fourier transform. Functions of τ are always defined as vanishing on the negative semiaxis, so that

$$f(\omega) = \int_0^\infty d\tau\, e^{-i\omega\tau} f(\tau)\,,$$

and ω will be understood to have a small negative imaginary part whenever it is necessary to assure the convergence of the Fourier integral.