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SENSITIZED FLUORESCENCE IN CROSSED ATOMIC BEAMS:

$$Hg^*(6^3P_{0,2}) + Tl(6^2P_{1/2})$$

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ABSTRACT

A velocity selected Tl beam has been crossed by an electron - bombarded Hg beam which contains a small percentage of the $Hg^*(6^3P)$ metastable levels (an approximate 5:1 ratio of $^3P_2$: $^3P_0$). By means of an interference filter - photomultiplier combination beneath the collision zone, the cross section for collisional production of the 5350Å ($7^2S_{1/2} \rightarrow 6^2P_{3/2}$) Tl fluorescence has been determined to increase monotonically with decreasing relative collision speed, g, approximately as g^{-s} for s = 2.0±0.5.

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Implications of these results for the sensitized fluorescence phenomenom in vapor mixtures of metallic elements are briefly discussed.

The pioneering work of Cario and Franck[1] demonstrated the sensitized fluorescence of Tl vapor by $Hg^*(^3P_1)$. Similar studies on this and related systems over the following 50 years have demonstrated relatively large cross sections at thermal collision energies for non-resonant excitation transfer between a variety of metal atoms.[2] Typically, these experiments consist of irradiating a cell containing a vapor mixture of atoms A and B by a resonance line of A and observing fluorescence from B^*. Quantitative interpretation of these experiments has been hampered, however, by uncertainties regarding the roles of resonance line broadening, radiation imprisonment, metastable states, and even weakly bound diatomic molecules.[3] The crossed beam technique would appear ideally suited to circumventing these difficulties, and this paper reports a crossed beam determination of the energy dependence of the cross section for $Hg^*(^3P_{0,2}) + Tl \rightarrow Hg + Tl^*$.

APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus and data analysis procedures are described in detail in Ref. 4. Atomic beams of Tl and Hg, prepared in conventional stainless steel dual-chamber source ovens, intersect

at 90°. Between source and beam intersection region (BIR), the Hg beam traverses an electron bombardment region where ~ 0.01% (rough estimate) is excited to the long-lived $Hg^*(^3P_{0,2})$ metastable levels, and the Tl beam traverses a slotted-disk velocity selector ($\Delta v/v = 0.22$ FWHM). Upon exiting the BIR, the Tl flux for the nominal velocity selector setting, $F_{Tl}(v_o)$, and the metastable Hg^* flux, F_{Hg^*}, are measured (in arbitrary units), respectively, by surface ionization on a heated tungsten filament and Auger electron ejection from a continuously-deposited K surface.

The BIR is enclosed within a light-tight cylinder, equipped with beam entrance and exit slits, which houses a spherical mirror above and a set of quartz lenses below the BIR. These serve to focus any photons emitted from a photon collection sphere (PCS, ~0.5 cm. radius, centered on BIR) within ~ ± 25° of a normal to the beams plane onto an interference filter chosen to isolate some particular atomic line; S_ν, the number of photons per second transmitted by the filter, are subsequently counted by means of an EMI-9558-QB photomultiplier tube. In order to determine the true atomic fluorescence rate, S_F, it is necessary to correct S_ν for two sources of backgound photons. Square-wave modulation (typically at ~ 40 Hz) of the electron beam and thus the $Hg^*(^3P_{0,2})$ discriminates against the DC photon background, which is largely due to the hot surface ionization filament. Periodic beam-flag interruption of the Tl beam permits correction

for a second component of the photon background which is proportional to $F_{Hg}*$ and is presumably $Hg^*(^3P_1)$ fluorescence at 2537Å, produced by inelastic collisions of $Hg^*(^3P_2)$ with ambient background gas, which partially penetrates the interference filter shield.

RESULTS

Figure 1 shows a Tl energy level diagram. The 5350Å($7^2S_{1/2} \rightarrow 6^2P_{3/2}$) Tl fluorescence line was chosen for quantitative study because (1) the $F_{Hg}*$ dependent photon background rendered study of shorter wavelength lines more difficult and (2) ambiguities due to a possible anisotropic photon angular distribution were eliminated by selection of a transition originating from a J = 1/2 level. Figure 2 summarizes the results of analyzing the collected data as

$$Q'_{rel}(g) = S_F v_o v'_{Hg}*/F_{Hg}*F_{Tl}(v_o)g \qquad (1)$$

where Q'_{rel} is the apparent cross section in arbitrary units for excitation of 5350Å Tl fluorescence in collision of a ground state Tl with a metastable Hg^* atom, $g = (v_o^2 + v'^2_{Hg}*)^{1/2}$ is the asymptotic relative collision speed, and $v_{Hg}*$ is the most probable Hg^* speed. Since the excitation efficiency of the electron gun is considerably less than unity corresponding to an excitation probability inversely proportional to speed, an assumed thermal Hg speed distribution results in $v'_{Hg}* = (kT_{Hg}/m_{Hg})^{1/2}$. In interpreting the data [4b], we have adopted a procedure wherein an assumed functional form of the true inelastic collision cross section, Q(g), is convoluted over the Hg^* and Tl speed distributions[5] to

predict a value for S_F; this is then treated according to Eq. (1) to yielded a predicted $Q_{rel}(g)$ for comparison with the experimental $Q'_{rel}(g)$. In practice, however, this deconvolution procedure is hardly worthwhile because the computed $Q_{rel}(g)$ typically differs insignificantly from the assumed form of $Q(g)$.

The following experimental checks were performed in order to insure that the data of Fig. 2 do indeed represent the cross section for $H_g^*(^3P_{0,2})$ + Tl production of 5350Å Tl fluorescence.

(1) The bandpass window of the interference filter is temperature sensitive. Thus, it proved necessary to circulate room temperature water through the filter mount in order to prevent its cooling as a result of the extensive liquid nitrogen shielding employed in the vacuum chamber. Auxiliary experiments established that S_F dropped to zero if this water circulation system was disconnected. Thus, the interference filter did successfully isolate the 5350Å Tl fluorescence line.

(2) At a sufficiently low Tl source pressure ($\sim 5 \times 10^{-4}$ torr), the measured Tl speed distribution followed the Maxwell-Boltzman equation. This provided an absolute velocity selector calibration and also insured against a background pressure attenuation of the Tl beam, an implicit assumption in Eq. (1).

(3) As a function of electron gun energy, F_{Hg}^* exhibits a threshold at ~3V and a peak at 5.3V; a second peak

appears at ~IIV. Only this higher peak persists if the K Auger electron ejection surface is replaced by an Hg surface. This agrees with observations of other workers[4] and indicates that an electron gun setting of 5.3 V, where the fluorescence data of Fig. 2 was collected, corresponds to excitation of the relatively low energy $Hg^*(6^3P_{0,2})$ metastable levels. An auxiliary experiment established that 5350Å fluorescence (at $g = 4.5 \times 10^4$ cm/sec) dropped rapidly as the electron energy was raised to 8V, demonstrating that it was produced by Tl colliding with these Hg^* levels. The electron gun is operated at the space charge limit so that it is not possible to resolve $Hg^*(6^3P_o)$ and $Hg^*(6^3P_2)$ production. Using data in the literature on electron excitation of Hg, we estimate an approximately statistical 5:1 ratio of $^3P_2$:^3P_o at 5.3 V.

(4) Using estimated detection efficiencies, the absolute values of S_F, $F_{Tl}(v_o)$, and $F_{Hg}*$ would correspond to $Q'_{rel} \approx 4 Å^2$ at $g = 5 \times 10^4$ cm/sec. This estimate, which should be reliable to within a factor of ten, precludes the possibility that the observed fluorescence could have been produced by some minor beam constituent (e. g., Tl_2 or $Tl^*(6^2P_{3/2})$).

(5) The observed 5350Å fluorescence might arise by collisional production of $Tl^*(7^2S_{1/2})$ and/or some higher Tl^* level which would have a probability γ of populating $Tl^*(7^2S_{1/2})$ via photon emission. Table I presents some γ values obtained from Tl oscillator strength calculations.[6] Although an attempt at a quantitative study of the 2918/2921Å ($7^2D_{5/2,3/2} \rightarrow 6^2P_{3/2}$) fluorescence lines proved unsuccessful[7], the magnitude of the observed fluorescence indicated that[8] $Q'_{rel}(2918/2921Å)/Q'_{rel}(5350Å) \approx 0.05$. Since $\gamma(7^2D_{5/2}) \approx 0.1$ and $\gamma < 0.01$ for $7^2D_{3/2}$, $6^2D_{5/2}$, and $6^2D_{3/2}$, the observed 5350Å fluorescence must be due to collisional production of some S or P level.[9] Of these, the $7^2S_{1/2}$, $7^2P_{1/2}$,

and/or $7^2P_{3/2}$ are more likely to be produced by $Hg^*(6^3P_o)$ whereas the higher levels would be due to $Hg^*(6^3P_2)$; in view of the entries in Table I and the likelihood that the beam is richer in $Hg^*(6^3P_2)$, the 5350Å Tl fluorescence is probably about equally sensitive to participation of either metastable Hg^* level. Indeed, Fig. 1 suggests

$$Hg^*(6^3P_2) + Tl \rightarrow Hg + Tl^*(9^2S_{1/2})$$

as a prime candidate for the possible origin of the 5350Å fluorescence because the energy defect is only - 0.11eV. Again a quantitative study of the 2826Å ($9^2S_{1/2} \rightarrow 6^2P_{3/2}$) fluorescence line proved impossible, but the magnitude of the observed fluorescence indicated that[8] Q'_{rel}(2826Å)/(5350Å) $\approx$ 0.5. Since $\mathcal{A}$ ($9^2S_{1/2}$) = 0.2, collisional production of this level certainly doesn't dominate the observed 5350Å fluorescence.

(6) Implicit in Eq. (1) is the assumption that all Tl fluorescence originates in the LCS. This is certainly an excellent assumption in view of the size of the LCS and Tl speeds because all pertinent ^2S and ^2P Tl levels have radiative lifetimes shorter than 0.2 μsec.

DISCUSSION

Despite the uncertainties regarding the relative contributions of $Hg^*(6^3P_o)$ and $Hg^*(6^3P_2)$ as well as the identity of the collisionally produced Tl^* levels, the results obtained here provide some insight

into the nature of the excitation transfer process in this system and, by extrapolation, in the general sensitized fluorescence phenomenom in mixtures of metallic vapors, or at least in that subset which are initiated by metastable electronic states.

A propensity rule which is often cited states that the energy transfer efficiency increases with decreasing energy defect. The smallest energy defect in Fig. 1 occurs for the $Tl^*(9^2P_{1/2})$ level, only 0.04 eV above the $Hg^*(6^3P_2)$ level. However, it has proven impossible to fit any Q(g) function having a 0.04 eV threshold to the data of Fig. 2 since the calculated $Q_{rel}(g)$ curve always shows a peak at ~ 0.05eV. Since no break is apparent in $Q'_{rel}(g)$ in the vicinity of 0.05eV, the dominant inelastic process must produce Tl^* levels lower in energy than the reactant Hg^* level despite energy defects in excess of 0.1eV.

A perturbation treatment of the inelastic process based on the asymptotic energy defect for this system would predict[2b] a Q(g) which increased with increasing g over the range in g studied here. The contrasting behavior of the data of Fig. 2 emphasizes that any treatment of the inelastic process must incorporate a smaller energy defect between molecular electronic states formed at some point in the collision.[10]

The data of Fig. 2 are well fit by a cross section of the form $Q(g) \alpha g^{-s}$ for s = 2.0±0.5. Although of the same qualitative monotonic behavior, this is a steeper energy dependence than has been reported at low energies for some other inelastic electronic processes involving metal atoms.[11] Inelastic collisions of this type

have often been discussed, at least semi-quantitatively, in a Landau-Zener picture of reactant and product diabatic potential functions, $V_{11}(R)$ and $V_{22}(R)$, which intersect at some R_x. In this picture, the inelastic cross section becomes[12]

$$Q(g) = 4\pi R_x^2 [1 - V_{11}(R_x)/E] G(\lambda). \tag{2}$$

In the usual experimental situation, $E \gg V_{11}(R_x)$ and the energy dependence of Q is embodied in $G(\lambda)$. For the present low energy study, however, the energy dependence of Q appears to be dominated by the first term[13], the cross section for reactant penetration to R_x. The solid curve in Fig. 2 shows a fit of Eq. (2) obtained for $G(\lambda)$ assumed constant and $V_{11}(R_x) = -0.6$eV. This emphasizes that the data imply a strong attraction between reactants at separations larger than the region of strong mixing of electronic states.[14]

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7. Although very noisy, the data collected did suggest a flatter speed dependence of Q'_{rel}(2918/2921Å) than the behavior exhibited in Fig. 2.

8. These intensity ratio estimates are uncertain to within a factor of two or three since they are calculated by assuming that apparatus detection efficiencies are invariant from pump-down to pump-down.

9. Any F level must radiate through a D level.

10. H. F. Krause, S. Datz, and S. G. Johnson, J. Chem. Phys. 58, 367 (1973) make this same point in interpreting their measured velocity dependence of E → V transfer in $Hg^*(6^3P_2)$ collisions.

11. For example, see Ref. 10 and: (a) quenching of excited alkali atoms: B. L. Earl and R. R. Herm, J. Chem. Phys. 60, 4568 (1974); (b) CO^* + Hg: F. J. Van Itallie and R. M. Martin, Chem. Phys. Letters 17, 447 (1972).

12. R. E. Olson, F. T. Smith, and E. Bauer, Appl. Opt. 10, 1848 (1971).

13. This expression is actually valid only above some critical energy where the classical "orbiting" phenomenom is no longer operative; see Ref. 11a.

14. The observation that mercury sensitized fluorescence of a number of metal vapors efficiently excites many different transitions (Ref. 2) suggests that this attractive interaction is quite common. It is interesting to speculate that an ion-pair intermediate could account qualitatively for this attractive coupling of initial and final states. No stable Hg^- state exist, but a number of resonant states are known or expected; see, for example, C. E. Kayatt, J. A. Simpson, and S. R. Mielczarek, Phys. Rev. 138, A385 (1965) and R. J. Zollwig, J. Chem. Phys. 50, 4251 (1967).

Table I. Probability of 5350Å fluorescence from a Tl level (γ^{ℓ}).

Tl Level	$7^2S_{1/2}$	$8^2S_{1/2}$	$9^2S_{1/2}$	$7^2P_{1/2}$	$7^2P_{3/2}$	$8^2P_{1/2}$	$8^2P_{3/2}$	$7^2D_{5/2}$
γ^{ℓ}	1.0	0.2	0.2	1.0	1.0	0.4	0.6	0.1

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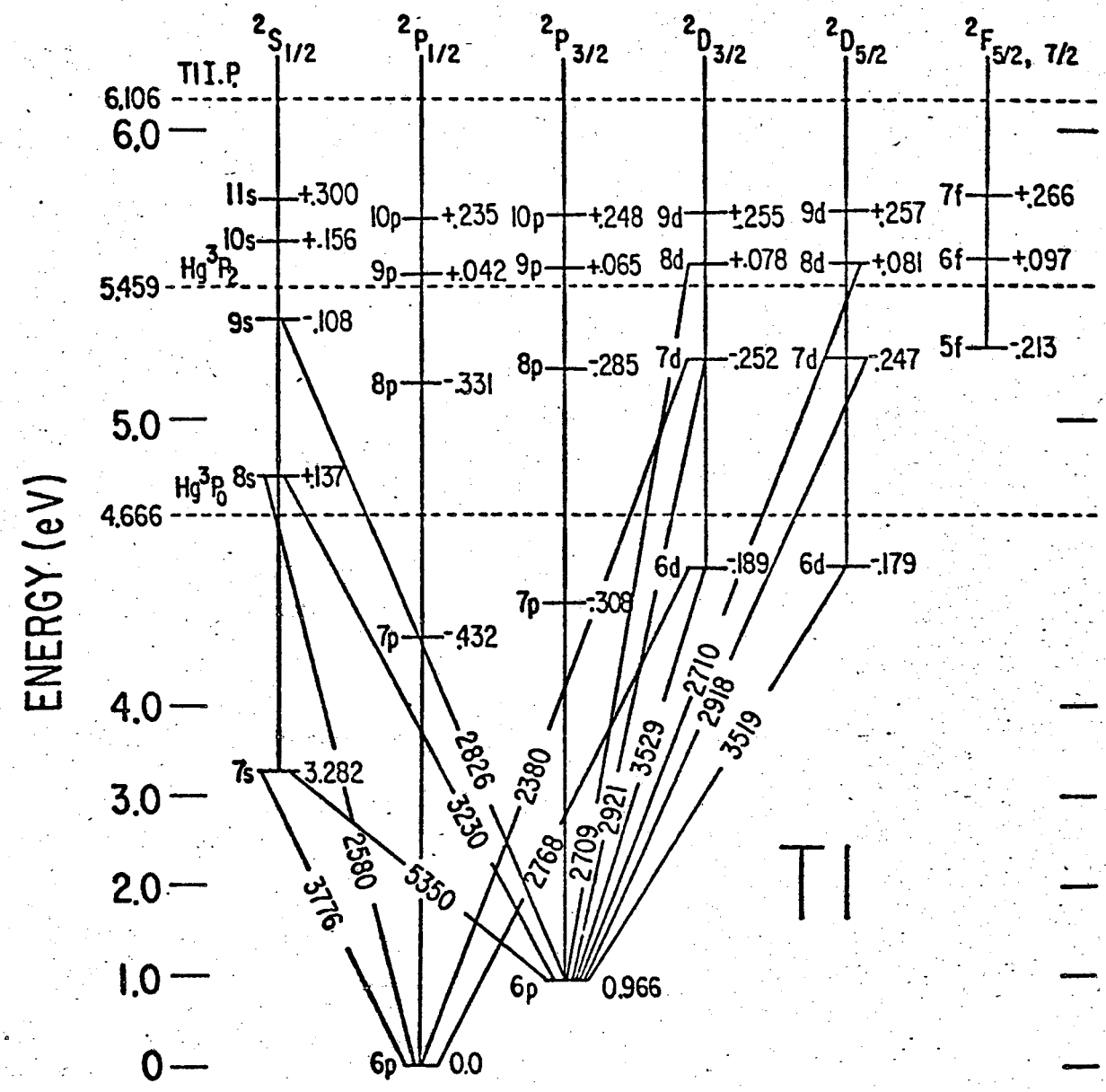
FIGURE CAPTIONS

Fig. 1. Thallium energy level diagram. (Levels corresponding to excitation of an inner 6 s electron are not germane to this experiment and are not listed.) All energies are given in electron volts. Energy above the ground state is given for Tl levels below 4 eV; for higher levels, the energy quoted is the energy defect (i. e., the energy separation of the Tl level from the nearest metastable Hg level). Energies of the $Hg^*(6^3P)$ metastable levels are shown as the two lower dashed lines; the Tl ionization limit is shown as the upper dashed line. Diagonal lines indicate prominent emission lines (in Å) reported in studies of $Hg^*(^3P_1)$ sensitized fluorescence of Tl.

Fig. 2. Data points show measured cross section for excitation of 5350Å$(7^2S_{1/2} \rightarrow 6^2P_{3/2})$ Tl fluorescence in collisions of $Tl(6^2P_{1/2})$ with $Hg^*(6^3P_{0,2})$. Data from separate experimental runs shown as different symbols; error bars represent standard deviations estimated by error propagation analysis. Solid curve shows a fit to the data for Q = constant $[1 - 2\, V_{11}(R_x)/\mu g^2]$ with $V_{11}(R_x) = -0.6$ eV.


$^2S_{1/2}$
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$^2D_{3/2}$
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Tl I.P.
6.106
6.0
5.459
5.0
4.666
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1.0
0
ENERGY (eV)
11s +.300
10s +.156
Hg^3P_2
9s -.108
Hg^3P_0 8s +.137
7s 3.282
10p +.235
9p +.042
8p -.331
7p -.432
6p 0.0
10p +.248
9p +.065
8p -.285
7p -.308
6p 0.966
9d +.255
8d +.078
7d -.252
6d -.189
9d +.257
8d +.081
7d -.247
6d -.179
7f +.266
6f +.097
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Fig. 1

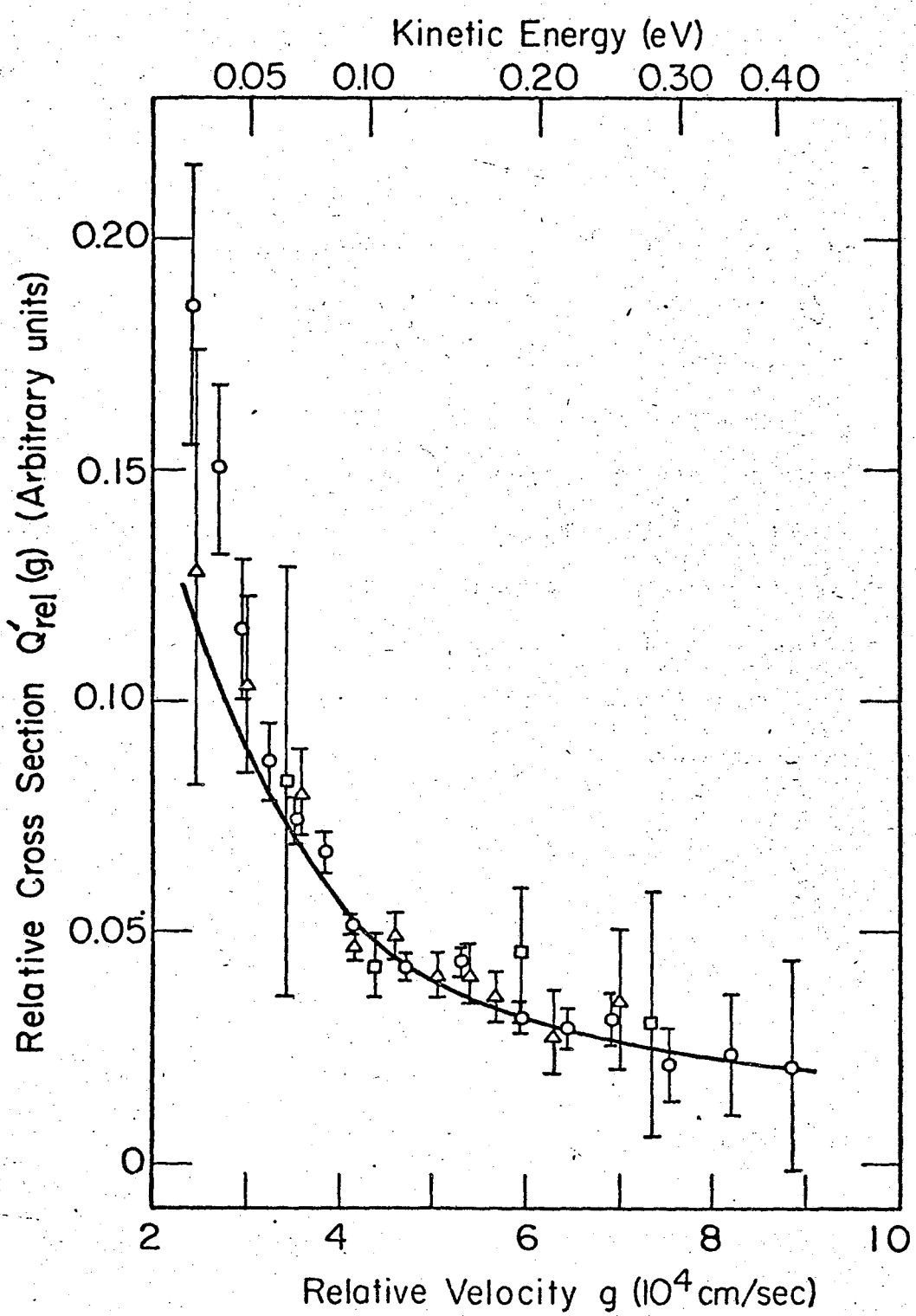

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Fig. 2

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