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F. H. M. FAISAL

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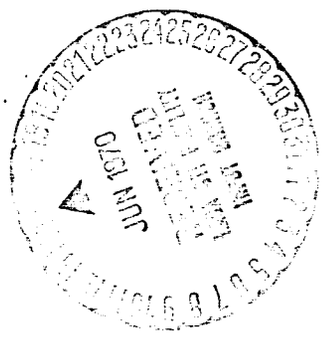

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GREENBELT, MARYLAND

Rotational Excitations of Molecules by Collision with Atoms

F. H. M. Faisal
Research Associate*
Laboratory for Space Physics
Goddard Space Flight Center
Greenbelt, Maryland

ABSTRACT

First order semi-classical scattering theory is used to estimate the rotational excitation cross-sections of N_2 by Ne impact. Results are compared with available quantal calculations. Linear trajectories are assumed for the heavy atomic projectiles. The solution is obtained analytically.

*Research Associate, National Academy of Sciences working on a Fellowship at Goddard Space Flight Center. On leave of absence from Pakistan Atomic Energy Commission, Karachi, Pakistan.

1. Introduction

Investigations of heavy-particle collisions at thermal energies are recently being carried out with considerable interest. They are important for an understanding of the various collisional processes leading to relaxations, heat conductions and eventually chemical reactions involving simple gases. Complete quantum mechanical calculations of such processes (including the elementary but fundamental process of energy transfer by collisional excitations of simplest molecules by atomic projectiles) are extremely involved. This is mainly due to the presence of large (indeed infinite) degrees of freedom in the form of vibrational-rotational states of the system. Nevertheless, attempts have already been made and very interesting results obtained in some cases by elaborate quantum mechanical calculations (Bernstein et al., 1963; Burke et al., 1969).

For certain purposes, however, it may be sufficient to obtain an approximate estimate of such cross-sections and their trends only if it could be achieved by a simple and rapid method of calculation. To this effect, we investigate here the collisional excitations of rotational states of a diatomic molecule by atomic projectiles, using the first order time-dependent scattering theory within a semi-quantal framework. This method was first used in atomic excitation problems by Seaton (1962) and subsequently by many others. In the semi-quantal method the target system is treated quantum mechanically while the motion of the projectile is considered along a classical trajectory. In the end, however, we attempt to incorporate the quantum nature of the projectile motion by demanding the cross-sectional expression to satisfy rigorous quantum mechanical symmetry properties.

2. Theory

The first order transition amplitude between the states i and f can be given, within the time-dependent scattering theory (Dirac, 1926, 1927) by

$$b_{if} = -i \langle i | \int_{-\infty}^{\infty} V(t)\, dt \,| f \rangle \tag{1}$$

where V(t) is the time-dependent interaction (responsible for the transition) between the projectile atom at p and the target molecule AB (Fig. 1).

In general the interaction may be written down as a multiple expansion of the form

$$V(r_p(t)) = V_0(r_p(t)) + V_2(r_p(t))\, P_2(\cos\theta_p(t)) + \cdots \tag{2}$$

where $V(\vec{r}_p(t)) \equiv V(t)$ is given by the projectile-trajectory equations. In Fig. 1 we choose our laboratory coordinate system with the z'-axis along direction of the incoming beam (as in the usual experimental setup). Let the molecular axis be along the z-direction of a set of coordinates fixed to the target body. The angle θ_p is between the axis z, and the position vector $\vec{r}_p$ of the projectile, measured from the center of mass of the molecule. The c.m. is chosen as the common origin of the two-sets of reference axes.

We consider that the molecule is rotating around the laboratory-axis and hence the rotational wave-functions may be written down as

$$\begin{aligned} |i\rangle &= |j_i\, m_i\, k_i\rangle \\ &= \left(\frac{2j_i+1}{8\pi^2}\right)^{\frac{1}{2}} D^{(j_i)*}_{m_i,k_i}(\alpha,\beta,\gamma) \end{aligned} \tag{3}$$

where D's are the well-known Wigner rotation matrices (Edmonds, 1960) with the Euler angles α, β, γ as arguments, which specify the orientation of the molecular axis with respect to the laboratory axes. The indices j, m, k are, respectively, the rotational quantum number and its projections on the laboratory-axis z' and the body-fixed axis z . We note that if the target is in the state Σ, then $k_i = 0$. We further note that for transitions between states j_i and j_f ($j_i \neq j_f$) the spherical part $V_o(r_p)$ of (1) does not contribute to the cross-section, due to the orthogonatily between different rotational states. Thus for the process

$$|j_i\, m_i\, k_i\rangle \longrightarrow |j_f\, m_f\, k_f\rangle$$

using (3) in (1), we find for the transition amplitude

$$b_{if} = \left\{\frac{(2j_i+1)(2j_f+1)}{8\pi^2}\right\}^{\frac{1}{2}} \times$$

$$\times \sum_\lambda \left\langle D^{(j_f)}_{m_f,k_f} \middle| \int_{-\infty}^{\infty} V_\lambda(r_p) P_\lambda(G,\theta_p)\, dt \middle| D^{(j_i)*}_{m_i,k_i} \right\rangle \qquad (4)$$

where

$$P_\lambda(G,\theta_p) = \frac{4\pi}{2\lambda+1} \sum_\mu Y^{*\mu}_\lambda(\theta_p,\phi_p)\, Y^{\mu}_\lambda(\beta,\alpha)$$

and β,α become the polar coordinates of the molecule referred to the laboratory frame.

Using the usual symmetry properties and the integral of three D matrices (Edmonds, 1960) we find

$$b_{if} = \sum_\lambda \left\{\frac{4\pi}{2\lambda+1}(2j_i+1)(2j_f+1)\right\}^{\frac{1}{2}} (-1)^{m_i-k_i} \times$$

(5)

$$\times \begin{pmatrix} j_f & \lambda & j_i \\ k_f & 0 & -K_i \end{pmatrix} \sum_{\mu} (-1)^{\mu} \begin{pmatrix} j_f & \lambda & j_i \\ m_f & \mu & -m_i \end{pmatrix} \times I_{\lambda\mu} \qquad 5$$

where

$$I_{\lambda\mu} = \int_{-\infty}^{\infty} V_{\lambda}(r_p(t))\, Y_{\lambda}^{\mu}(\theta_p(t), \varphi_p(t))\, dt \qquad (6)$$

Taking the modulus square of the amplitude (5) and summing of over the final m_f states and averaging over the initial m_i states, we obtain for the differential cross-section

$$\frac{d\sigma}{d\Omega} = \frac{1}{(2j_i+1)} \sum_{m_i, m_f} |b_{if}|^2$$
$$= \sum_{\lambda} \frac{4\pi}{(2\lambda+1)^2} (2j_f+1) \begin{pmatrix} j_f & \lambda & j_i \\ K_f & 0 & -K_i \end{pmatrix}^2 \left\{ \sum_{\mu} I_{\lambda\mu} \right\}^2 \qquad (7)$$

where the differential solid-angle $d\Omega$ can be written for straight line trajectories as $2\pi b db$ where b is the usual impact parameter.

Integrating over the impact parameter b one obtains for the total cross-section

$$\sigma = 8\pi^2 \sum_{\lambda} \frac{2j_f+1}{(2\lambda+1)^2} \begin{pmatrix} j_f & \lambda & j_i \\ K_f & 0 & -K_i \end{pmatrix}^2 \times I_{\lambda}(b_0) \qquad (8)$$

where

$$I_{\lambda}(b_0) = \frac{\pi}{v^2} \int_{b_0}^{\infty} \left\{ \sum_{\mu} I_{\lambda\mu}(b) \right\}^2 b\, db \qquad (9)$$

The quantity b_0 is a cutoff parameter of the order of atomic dimensions (Seaton, 1962), introduced in place of the lower limit o in the integral (8), which otherwise yields infinite cross-sections (for straight line trajectories) with $b_0 = 0$.

3. Numerical Calculations

To obtain numerical results for Ne-N_2 collisions we use the potential energy curve adopted by Burke et al. (1969) for the same system. The effective interaction obtained by semi-emperical considerations by the above authors is given explicitly in atomic units to be

$$V(\vec{r}_p(t)) = \left(\frac{1}{r_p(t)}\right)^{12}\left(1972224 + 739584\, P_2(\cos\theta_p(t))\right) - \left(\frac{1}{r_p(t)}\right)^{6}\left(37.7947 + 6.65187\, P_2(\cos\theta_p(t))\right). \tag{12}$$

The corresponding reduced mass and the moment of inertia of the target are respectively

$$m_o = 2.1387 \times 10^4 \quad \text{(a.u.)}$$

$$I = 5.442 \times 10^4 \quad \text{(a.u.)}$$

For transitions between unequal rotational quantum states, the spherical part of (12) does not contribute to the cross-section and thus the interaction responsible for such transitions essentially becomes

$$V(t) = \left(\frac{C_{12}}{r_p^{12}(t)} - \frac{C_6}{r_p^{6}(t)}\right) P_2(\cos\theta_p(t)) \tag{13}$$

where $C_{12} = 739584$ (a.u.) and $C_6 = 6.65187$ (a.u.).

We have assumed the trajectory of the projectile to be linear along the beam direction z' and hence we can write the trajectory equations to be

$$\begin{aligned} r_p'^2(t) - r_p^2(t) &= b^2 + v^2t^2 \\ \cos\theta_p(t) &= \frac{vt}{r_p'} \\ \varphi_p(t) &= 0 \end{aligned} \tag{14}$$

From equation(8)we notice that the cross-section depends on the integrals $I_{\lambda\mu}$ defined in (6).

Substituting (14) and (13) in (6) and performing the integration over t we find that the quantity

$$\sum_{\lambda=-2}^{2} I_{2\lambda}(b) = \left\{ \binom{10}{5} C_{12} \frac{\pi}{(2b)^{11}} - \binom{4}{2} C_6 \frac{\pi}{(2b)^5} \right\} \sqrt{\frac{15}{\pi}} \cdot \frac{1}{v}$$
$$+ \left\{ \binom{12}{6} C_{12} \frac{\pi}{(2b)^{13}} - \binom{6}{3} C_6 \frac{\pi}{(2b)^7} \right\} \times$$
$$\times \left\{ \frac{b^2}{v} \sqrt{\frac{15}{\pi}} \left(1 - \sqrt{5/4}\right) \right\} \qquad (15)$$
$$= -\frac{\sqrt{\pi}}{v} \left\{ \frac{a_0}{b^{11}} + \frac{a_1}{b^5} \right\}$$

where $a_0 = 1.5215 \times 10^5$ (a.u.)

$a_1 = -2.1492$ (a.u.)

Restricting ourselves to the dominant quadrupole term, $\lambda = 2$, we find from (15) and (9),

$$I_2(b_0) = \frac{\pi}{v^2} \int_{b_0}^{\infty} \left(\frac{a_0}{b^{11}} + \frac{a_1}{b^5} \right)^2 b\,db$$
$$= \frac{\pi}{v^2} \left[\frac{a_0^2/20}{b_0^{20}} + \frac{a_0 a_1/7}{b_0^{14}} + \frac{a_1^2/8}{b_0^8} \right] \qquad (16)$$

Thus the total cross-section given by (8) becomes

$$\sigma = 8\pi^2 \frac{2j_f+1}{25} \cdot \begin{pmatrix} j_f & 2 & j_i \\ 0 & 0 & 0 \end{pmatrix}^2 I_2(b_0) \qquad (17)$$

In (17) we have set $k_i = k_f = 0$ for the ground state of the target N_2 is a Σ state. The transition cross-section between any two states j_i and j_f is thus seen to be governed essentially through the 3-j symbol appearing in (17).

We immediately conclude that for finite probability of transitions the rotational quanta must change at least by two units of angular momenta. The cross-section as given by (17) is found to depend inversely as the square of the velocity of the projectile.

Before computing numerical results we shall, however, proceed further and apply the quantum mechanical symmetry properties to be satisfied by the cross-sectional expressions in general and modify equation (17) accordingly.

4. The Symmetrisation of Cross-Sections

From the principle of detailed balance we require that the cross-section of a process, σ_{if}, and its inverse, σ_{fi}, must be related by the relation

$$\omega_i \, v_i^2 \, \sigma_{if} = \omega_f \, v_f^2 \, \sigma_{fi}$$

where ω_i and ω_f are the statistical weights and v_i and v_f are the velocity in a.u. for the initial state i and the final state f, respectively. For the rotational states $\omega_i = 2j_i + 1$ and $\omega_f = 2j_f + 1$; we therefore find that σ_{if} must be of the form

$$\sigma_{if} = \frac{v_f}{v_i} \sqrt{\frac{2j_f+1}{2j_i+1}} \times \text{(cross-sectional expression symmetric in i and f)} \qquad (18)$$

We shall furthermore require that the projectile velocity be symmetried for the initial and final motions which are in general different in energy. This is best achieved by invoking the correspondence principle as beautifully discussed in Biedenharn and Brussaard (1965) and replacing v by the relation

$$v \longrightarrow \left(v_i v_f \; \frac{v_i + v_f}{2} \right)^{\frac{1}{3}} \qquad (19)$$

Substituting (19) and the cross-sectional expression (17) in equation (28) we finally obtain for the symmetrised cross-section

$$\sigma_{if} = \frac{8\pi^2}{25} \frac{2j_f+1}{} \begin{pmatrix} j_f & 2 & j_i \\ 0 & 0 & 0 \end{pmatrix}^2 \frac{v_f}{v_i} \left(v_i v_f \; \frac{v_i + v_f}{2} \right)^{-2/3} \times I_2(b_0) \, , \qquad (20)$$

(πa_0^2)

5. Results and Discussions

In Table I we have presented results for the transitions $j \rightarrow j' = 0 \rightarrow 2$; $2 \rightarrow 4$; and $4 \rightarrow 6$; and in Table II for $j \rightarrow j' = 1 \rightarrow 3$; and $3 \rightarrow 5$, for incident energies between 1×10^{-3} to 45×10^{-3} a.u.

In the present calculation we are essentially interested in the order of magnitude estimates of the cross-sections and shall not attempt to choose the 'best value' of the parameter b_o. One way of doing this would be to normalize the results at higher energies with that obtained from quantal calculations or from experimental values if available.

Instead we have made here the simple choice of the cut-off parameter (Fig. 2) $b_o = 5.75$ (a.u.), equal to the approximate 'hard core' radius of the Ne-N_2 potential, which determines the distance of closest approach of the colliding system.

The results for the $0 \rightarrow 2$ transition in the above energy range is found to be comparable with that obtained by the detailed quantal calculation of Burke et al. (1969). In Fig. 3 we also find that $\log \sigma_{0_2}(E_1)$ vs. $E_1^{\frac{1}{2}}$ behaves numerically as an approximate straight line as observed in the above reference. In general the Tables show that at a given energy the cross-sections for transitions between higher angular momenta are smaller than those between the lower ones. We shall point out that in the present approximation although the cross-sections vanish at the thresholds as they should, it tends to give too large cross-sections at rather low energies. This may be expected of the straight line approximation which is less appropriate for lower energies. One possible way of improving the situation

would be to replace the straight line motion by trajectories calculated numerically in the central part of the Lennard-Jones 12-6 potential for the system.

This, however, would cost us in terms of loosing the extreme simplicity of the present analytic calculation.

Table I

Total Cross-Sections $\sigma_{jj'}(E_i)$ in πa_o^2

E_i	$\sigma_{o_2}(Ei)$	$\sigma_{24}(Ei)$	$\sigma_{46}(Ei)$
0.10000D-02	0.48318D 01	0.24841D 01	0.21941D 01
0.11000D-02	0.43926D 01	0.22585D 01	0.19950D 01
0.12000D-02	0.40266D 01	0.20704D 01	0.18291D 01
0.13000D-02	0.37169D 01	0.19112D 01	0.16886D 01
0.14000D-02	0.34514D 01	0.17747D 01	0.15681D 01
0.15000D-02	0.32213D 01	0.16565D 01	0.14636D 01
0.16000D-02	0.30200D 01	0.15530D 01	0.13722D 01
0.17000D-02	0.28424D 01	0.16816D 01	0.12916D 01
0.18000D-02	0.26845D 01	0.13805D 01	0.12199D 01
0.19000D-02	0.25432D 01	0.13078D 01	0.11557D 01
0.20000D-02	0.24160D 01	0.12424D 01	0.10980D 01
0.21000D-02	0.23010D 01	0.11833D 01	0.10457D 01
0.22000D-02	0.21964D 01	0.11295D 01	0.99818D 01
0.23000D-02	0.21009D 01	0.10804D 01	0.95480D 00
0.24000D-02	0.20134D 01	0.10354D 01	0.91503D 00
0.25000D-02	0.19328D 01	0.99398D 00	0.87844D 00
0.26000D-02	0.18585D 01	0.95576D 00	0.84467D 00
0.27000D-02	0.17897D 01	0.92036D 00	0.81339D 00
0.28000D-02	0.17258D 01	0.88750D 00	0.78435D 00
0.29000D-02	0.16662D 01	0.85790D 00	0.75731D 00
0.30000D-02	0.16107D 01	0.82834D 00	0.73207D 00
0.31000D-02	0.15587D 01	0.80162D 00	0 70846D 00
0.32000D-02	0.15100D 01	0.77657D 00	0.68632D 00
0.33000D-02	0.14643D 01	0.75304D 00	0.66553D 00
0.34000D-02	0.14212D 01	0.73089D 00	0.64596D 00
0.35000D-02	0.13806D 01	0.71001D 00	0.62751D 00
0.36000D-02	0.13423D 01	0.69029D 00	0.61008D 00
0.37000D-02	0.13060D 01	0.67163D 00	0.59359D 00
0.38000D-02	0.12716D 01	0.65396D 00	0.57797D 00
0.39000D-02	0.12390D 01	0.63719D 00	0.56315D 00
0.40000D-02	0.12080D 01	0.62126D 00	0.54908D 00
0.41000D-02	0.11786D 01	0.60611D 00	0.53569D 00
0.42000D-02	0.11505D 01	0.59168D 00	0.52293D 00
0.43000D-02	0.11238D 01	0.57792D 00	0.51077D 00
0.44000D-02	0.10982D 01	0.56479D 00	0.49917D 00
0.45000D-02	0.10738D 01	0.55224D 00	0.48807D 00

N.B. Numbers following D are powers of 10 to be multiplied with.

Table II

Total Cross-Sections $\sigma_{jj'}(Ei)$ in πa_o^2

Ei	$\sigma_{13}(Ei)$	$\sigma_{35}(Ei)$
0.10000D-02	0.28987D 01	0.22995D 01
0.11000D-02	0.26353D 01	0.20907D 01
0.12000D-02	0.24158D 01	0.19166D 01
0.13000D-02	0.22300D 01	0.17693D 01
0.14000D-02	0.20707D 01	0.16430D 01
0.15000D-02	0.19327D 01	0.15336D 01
0.16000D-02	0.18119D 01	0.14378D 01
0.17000D-02	0.17054D 01	0.13532D 01
0.18000D-02	0.16106D 01	0.12781D 01
0.19000D-02	0.15259D 01	0.12109D 01
0.20000D-02	0.14496D 01	0.11503D 01
0.21000D-02	0.13806D 01	0.10956D 01
0.22000D-02	0.13178D 01	0.10458D 01
0.23000D-02	0.12605D 01	0.10003D 01
0.24000D-02	0.12080D 01	0.95866D 00
0.25000D-02	0.11597D 01	0.92032D 00
0.26000D-02	0.11151D 01	0.88493D 00
0.27000D-02	0.10738D 01	0.85216D 00
0.28000D-02	0.10354D 01	0.82173D 00
0.29000D-02	0.99973D 00	0.79340D 00
0.30000D-02	0.96641D 00	0.76696D 00
0.31000D-02	0.93524D 00	0.74222D 00
0.32000D-02	0.90601D 00	0.71903D 00
0.33000D-02	0.87856D 00	0.69724D 00
0.34000D-02	0.85272D 00	0.67674D 00
0.35000D-02	0.82836D 00	0.65740D 00
0.36000D-02	0.80535D 00	0.63914D 00
0.37000D-02	0.78358D 00	0.62187D 00
0.38000D-02	0.76296D 00	0.60551D 00
0.39000D-02	0.74340D 00	0.58998D 00
0.40000D-02	0.72481D 00	0.57523D 00
0.41000D-02	0.70714D 00	0.56121D 00
0.42000D-02	0.69030D 00	0.54784D 00
0.43000D-02	0.67425D 00	0.53510D 00
0.44000D-02	0.65892D 00	0.52294D 00
0.45000D-02	0.64428D 00	0.51132D 00

Note: Numbers following D are powers of 10 to be multiplied with.

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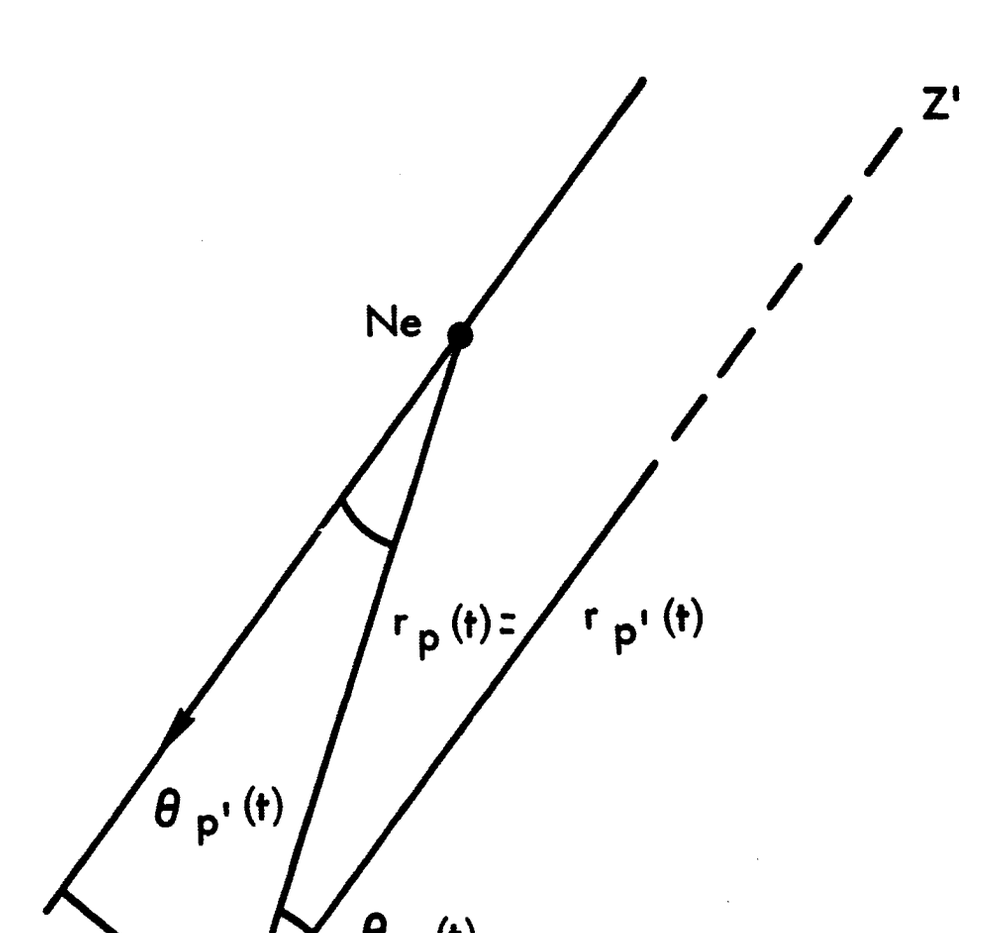


Figure 1

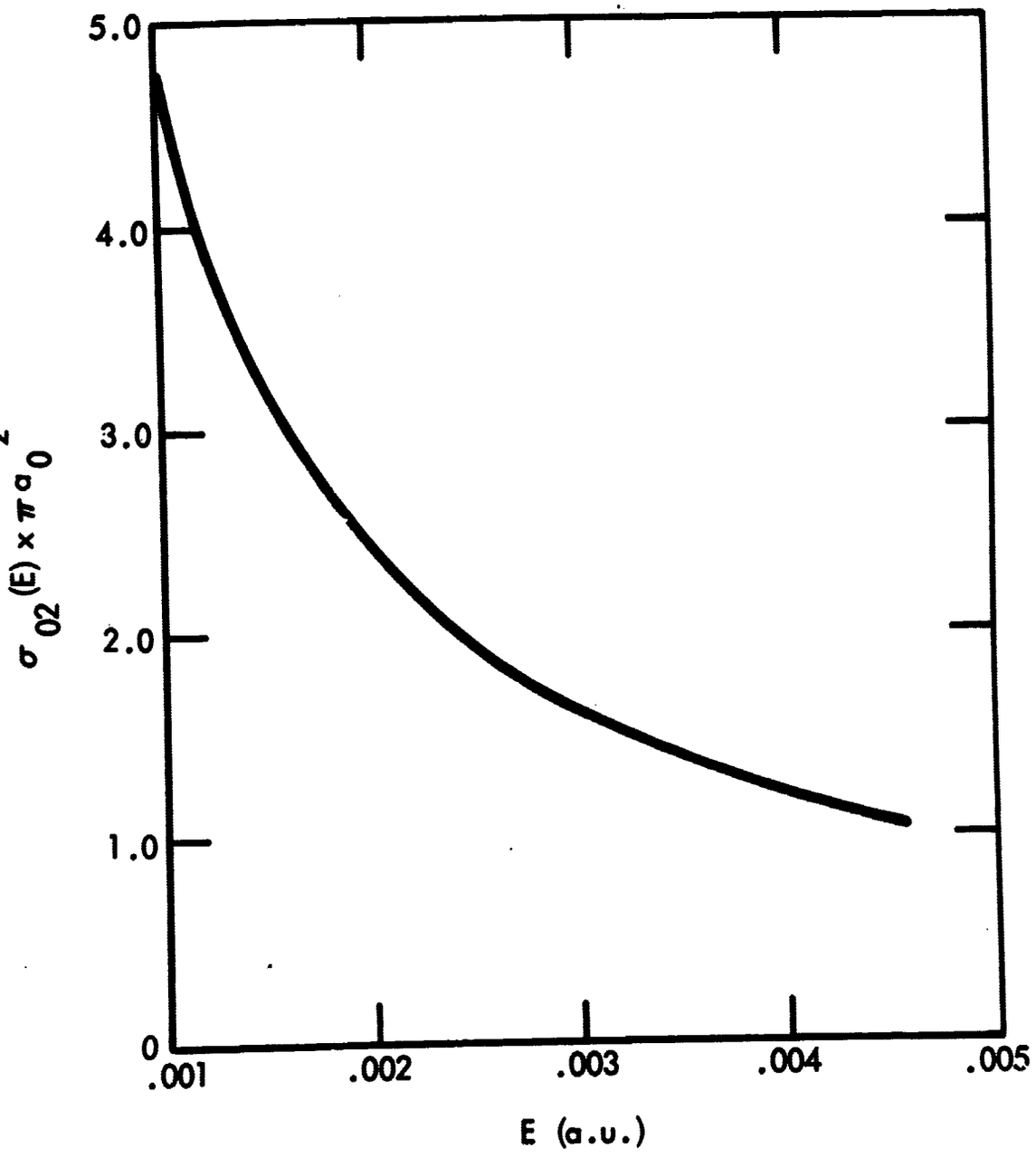
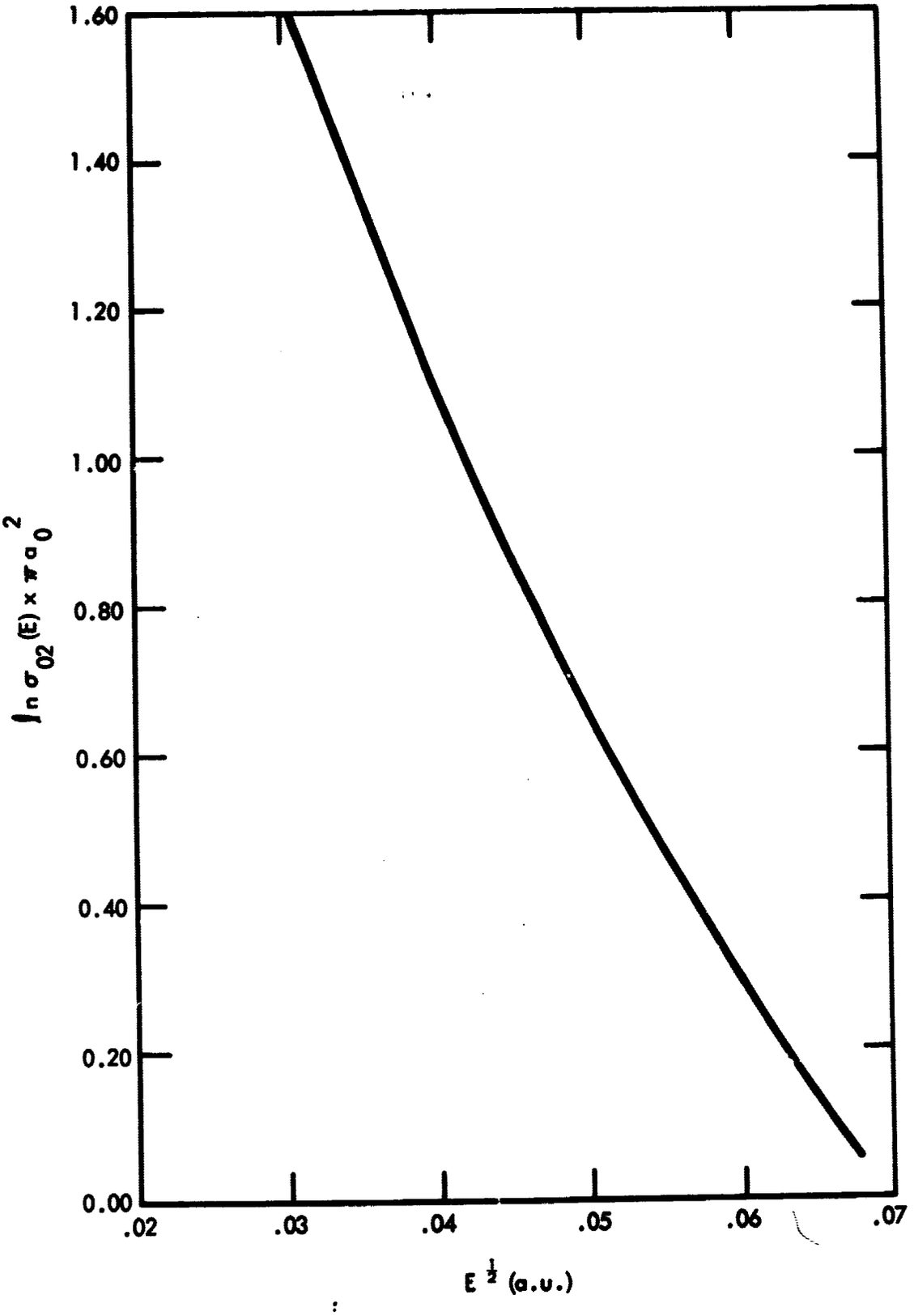


Figure 2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$\ln \sigma_{02}(E) \times \pi a_0^2$
$E^{\frac{1}{2}}$ (a.u.)

Figure 3