CALCULATED ELASTIC SCATTERING CROSS SECTIONS FOR THE H^+ - He SYSTEM[*]

by

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ABSTRACT

The *ab initio* computations by Michels and Harris, and Pyerimhoff, of the ground ($^1\Sigma^+$) state of HeH^+ provide a reliable interaction potential $V(r)$ to serve as a basis for prediction of proton-helium elastic scattering. This report summarizes calculations of total elastic cross sections, $Q(E)$, for low collision energies (E in the range 0.3 - 200 eV) where Q is sensitive primarily to the attractive part of $V(r)$. Superimposed upon the monotonic $E^{-1/3}$ dependence (arising from the long-range r^{-4} "tail" of the potential) are a number of broad extrema in $Q(E)$, characteristic of a potential well with the capacity for several (≥ 7) bound (vibrational) states.

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INTRODUCTION

The proton-helium system is one of the few for which a reliable *ab initio* interaction potential[1] is available to serve as a starting point for the calculation of scattering cross sections.[2] The early experimental measurements of "classical" total cross sections for H^+—He elastic scattering by Simons, Muschlitz and Unger[3] have been thoroughly analyzed (classically) by Mason and Vanderslice[4]. However, with the prospect of improved techniques for low energy ion beam scattering, yielding absolute "quantum" total (and differential) cross sections, it appears worthwhile to carry out the quantum calculations to serve as a guide to experiment.

The procedure employed is essentially that used previously[5] for the Li^+ —He system, altered to deal with the problem of interpolation of an accurate but "pointwise" potential function. For this purpose a seven-point inverse Aitken interpolation procedure[6] was used, which yielded the JWKBL phase shifts and thus the cross sections. The total cross section function $Q(E)$ exhibits a number of resolvable extrema (for $E < 150$ eV), superimposed on a monotonic $E^{-1/3}$ dependence.

PROCEDURES

Based on the best computed energies[1] of HeH^+ ($^1\Sigma^+$) (primarily those of Pyerimhoff[10]) a table of "best values" of $V(r)$ was constructed for $r < 5$ a.u.; for $r \geq 5$ a.u., the theoretical long-range functionality was assumed: $V(\text{a.u.}) = -0.6905/r^4(\text{a.u.})$. For the interval between successive points, designated, say, by N and $N+1$, a sixth-degree polynomial fit was used:

$$V_N(r) = \sum_{n=0}^{6} a_{Nn} r^n$$

where the coefficients a_{Nn} were determined by the seven points identified as $N-3, N-2, \ldots, N, N+1, \ldots; N+3$ (except near the ends of the range, where the coefficients were held constant). Table I (Appendix) lists the points and the matrix of the coefficients a_{Nn}. Figure 1 is a plot of the attractive part of the resulting "best" potential.

The JWKBL phase shifts were computed by methods essentially the same as in Ref. 5; the relations are summarized in the Appendix. JB phases were used when conditions for applicability were met.

The entire procedure was checked by performing phase shift and cross section computations on a "simulated" 35-point potential (points taken from the analytical potential V4 of

Ref. 5). Using the interpolation procedures described above, the potential, the phase shifts and the cross sections were reproduced satisfactorily (phases $\pm$ 0.02 rad., cross sections $\pm$ 1%). Unfortunately, for the H^+ - He case, exploratory tests showed a considerable sensitivity of the calculated cross sections to small changes in the potential in the region least accurately known (i.e., $4.5 < r < 5.5$ a.u.).

RESULTS AND DISCUSSION

The calculated cross sections are listed in Table II (Appendix) and plotted in Fig. 2. The dashed line represents the Schiff-Landau-Lifshitz- approximated[7] low-velocity behavior for an r^{-4} long-range potential. The ion-atom impact spectrum[5] ($C_{app.}$ vs. $1/v$) is shown in Fig. 3, with the extrema indexed in the usual manner. Since 7 maxima appear (down to the lower limit of the energy range, governed by considerations of orbiting-tunneling[5]) it is deduced[9] that the HeH^+ ($^1\Sigma^+$) well has a capacity for at least 7 bound (vibrational) states.

Both Fig. 2 and Fig. 3 show a slight bias in Q at the high-velocity end of the range, implying that the SLL approximation in this case becomes unsatisfactory at somewhat smaller velocities than for the Li^+ - He[5] system[8]. Only a small part of this deviation can be attributed to the previously-

mentioned sensitivity of the calculations to the (uncertainty in the) potential near the critical region near the r^{-4} tail.

The extrema-velocities (viz. Fig. 3) are quite stable to such small changes near the r^{-4} tail; this is as expected since the extrema-effect is known to be sensitive primarily to the potential near its minimum[9]. It is of interest to note from Fig. 2 that three extrema (N = 1, 1.5 and 2) appear at energies above 15 eV and should be readily observable with currently available ion-beam scattering techniques[10].

REFERENCES

1.(a) H. H. Michels and F. E. Harris, J. Chem. Phys. 39, 1464 (1963); (b) additional computations by H. H. Michels, private communication (Jan. 1965); (c) S. Pyerimhoff, J. Chem. Phys. 43, 998 (1965); (d) see also J. D. Stuart and F. A. Matsen, J. Chem. Phys. 41, 1646 (1964).

2. A notable exception is the well-studied He^+ - He system, for which the potential is fairly well known, and extensive, accurate low-energy scattering measurements (by (a) D. C. Lorents and W. Aberth, Phys. Rev. 139, A1017 (1965)) have been nicely analyzed theoretically: see (b) R. P. Marchi and F. T. Smith, Phys. Rev. 139, A1025 (1965). See also (c) W. Aberth, D. C. Lorents, R. P. Marchi and F. T. Smith, Phys. Rev. Letts 14, 776 (1965).

3. J. H. Simons, E. E. Muschlitz, Jr. and L. G. Unger, J. Chem. Phys. 11, 322 (1943). The data show suggestions of extrema, but since the measurements do not represent true total cross sections this is inconclusive. See also H. F. Helbig and E. Everhart, Phys. Rev. 136, A674 (1964) for related experiments involving charge transfer in the H^+ - He system.

4. E. A. Mason and J. T. Vanderslice, J. Chem. Phys. 27, 917 (1957); Chap. 17 of Atomic and Molecular Processes, D. R. Bates, ed., Academic Press, N.Y. (1962).

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5. G. G. Weber and R. B. Bernstein, J. Chem. Phys. 42, 2166 (1965).

6. G. G. Weber, Report WIS-TCI-79 (26 March 1965).

7. The low-velocity dependence is that of Eq. 8 of Ref. 5, implying the same Q for all $He-M^+$ systems at the same relative velocity.

8. This may be due to the relatively greater importance of the r^{-4} tail for the Li^+ - He potential than for the deeper H^+ - He well. In the former case, e.g., the hypothetical V4 for Li^+ - He, the r^{-4} dependence is well developed at a separation of less than twice the equilibrium distance, while for the H^+ - He case a separation of three to four times the equilibrium distance is required. This situation may well be the more typical one for real systems.

9. R. B. Bernstein and T. J. O'Brien, Disc. Far. Soc., 40, (in press); R. B. Bernstein, Science 144, 141 (1964) and previous references to the extrema-effect.

10. Recently, B. Bederson and co-workers have observed (private communication, Sept. 1965) an overall $E^{-1/3}$ behavior of the total cross section for the scattering of Cs^+ ions by Li at low energies.

APPENDIX

Table 1 lists the "best" potential for HeH^+ ($^1\Sigma^+$) together with the matrix of the coefficients a_{Nn} .

The relations used to compute the phase shifts and cross sections were the same as in Ref. 5, with the following changes:

In Eq. 4 the integral $I(z,y_o)$ is divided into two parts, from $z(=0.005)$ to $y_1(=0.2)$ and from y_1 to y_o.

The first interval, from z to y_1 , is divided into three equal intervals and the value of the integral in each interval is obtained by Gaussian quadrature (16 points) using for the function $f(y)$ the relation:

$$f(y) = 1 - \frac{D_3}{\epsilon T} \cdot y^4 - \beta^2 y^2$$

where $D_3 = 0.6905$ a.u., $\epsilon = 0.071446$ a.u., $T = A^2/B = E^*$ $B = 209.69$, $A = ka_o = 6.70835 \times 10^{-6} \times v$ (cm/sec).

The second part is divided into the intervals y_1 to y_2 , y_2 to y_3 , ..., y_n to y_o where y_i are the potential points considered as data. The value of the integral is obtained in each interval by Gaussian quadrature (16 points) using

$$f(y) = 1 - \frac{V(y)}{\epsilon T} - \beta^2 y^2$$

where

$$V(y) = a_{N0} + a_{N1} y^{-1} + a_{N2} y^{-2} + \dots a_{N6} y^{-6}$$

with

$$y \in [y(N), y(N+1)] \qquad \text{(as described above).}$$

The JB phase is:

$$\eta_{JB} = \frac{\pi}{8} D_3 B A^2 / \epsilon \cdot (\ell + \tfrac{1}{2})^3$$

The switch from η_{JWKBL} to η_{JB} occurs when

$$|\eta_{JWKBL} - \eta_{JB}| \leq 0.01 \text{ rad. } \underline{\text{and}} \quad \eta_{JWKBL} \leq 0.3 \text{ rad.}$$

Table 2 summarizes the results. Here

$$C_{app}(\text{erg cm}^4) = 4.07319 \times 10^{-54} \; Q \text{ (a.u.)} \times v \text{ (cm/sec)}$$

$$v \text{ (cm/sec)} = 1.49068 \times 10^5 \times A$$

and

$$E \text{ (eV)} = 4.17147 \times 10^{-13} \times [v \text{ (cm/sec)}]^2$$

The SLL-approximation would yield a constant value of

$$C_{app} = 2.36 \times 10^{-44} \text{ erg cm}^4 .$$

Table 1

Potential and Expansion Coefficients*

$$V(r) = \sum_{n=0}^{6} a_n r^n$$

r(a.u.)	V(r) (a.u.)	a_0	a_1	a_2
0.11495	13.414185	52.760074	-648.13326	3837.6207
0.19158	6.651966	52.760074	-648.13326	3837.6207
0.28737	3.528115	52.760074	-648.13326	3837.6207
0.37795	1.947813	52.760074	-648.13326	3837.6207
0.50000	.968010	29.350048	-255.39145	1201.5407
0.56669	.679897	-117.62215	1669.2700	-9095.4574
0.60000	.551980	650.76492	-6816.9393	29582.884
0.65000	.413993	-1075.1466	9979.0557	-38269.741
0.70000	.306146	423.46759	-3480.9968	11956.810
0.75000	.221388	45.56453	-333.7657	1073.6402
0.80000	.154531	-318.77484	2478.8701	-7942.4949
0.90000	.059937	1539.3273	-10864.835	31854.530
0.94487	.036751	-3874.1297	25433.326	-69261.700
1.00000	.000644	4911.3568	-29747.697	74817.799
1.05000	-.019089	-3400.1966	18993.438	-44066.481
1.10000	-.034706	611.03428	-3158.1138	6789.8621
1.20000	-.055710	6.2010594	-26.092787	50.454943
1.30000	-.066526	-16.270494	83.244958	-170.57446
1.40000	-.070914	11.440650	-43.669106	71.008525
1.45500	-.071446	5.5422261	-18.330646	25.737774
1.50000	-.071150	3.9365220	-11.826415	14.776572
1.60000	-.068770	3.2477774	-9.1836821	10.557843
1.70000	-.064820	3.7668820	-11.064265	13.390122
1.80000	-.060003	2.4706521	-6.6700414	7.2033616
2.00000	-.049525	2.1333858	-5.6166454	5.8385579
2.20000	-.039521	1.5208351	-3.8675196	3.7696875
2.50000	-.027102	1.0100012	-2.5471649	2.3579697
2.80000	-.018102	.54276842	-1.4655851	1.3225787
3.15000	-.011167	.071974721	-.49346068	.49290305
3.50000	-.006939	-.12056087	-.14063156	.22562954
4.00000	-.003661	-.12056087	-.14063156	.22562954
4.50000	-.002072	-.12056087	-.14063156	.22562954
5.00000	-.001105			

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* Since this table is intended only for illustrative purposes, the coefficients have been truncated to 8 figures; however, 12 figure accuracy is required in the actual computation in order to reproduce the potential points to the sixth decimal place.

a_3	a_4	a_5	a_6
-12641.342	23391.448	-22694.028	8976.6444
-12641.342	23391.448	-22694.028	8976.6444
-12641.342	23391.448	-22694.028	8976.6444
-12641.342	23391.448	-22694.028	8976.6444
-3538.7563	6267.5541	-5993.8944	2359.0477
25322.797	-38509.978	30522.194	-9886.4013
-67881.323	86819.636	-58697.602	16396.149
77777.338	-88431.689	53359.387	-13353.310
-21891.215	22497.279	-12296.166	2791.4055
-1889.9353	1893.5904	-1017.0085	227.96051
13471.323	-12777.009	6429.5088	-1341.4223
-49625.276	43311.417	-20076.164	3861.0015
100175.46	-81171.473	34942.126	-6243.6090
-100012.79	74944.082	-29850.110	4937.3557
54360.230	-37607.792	13835.318	-2114.5160
-7768.8685	4987.5188	-1703.0450	241.61280
-55.957361	36.197883	-12.642487	1.8393936
181.66359	-107.08766	33.307584	-4.2832008
-62.993887	31.950644	-8.7355492	1.0019197
-19.934158	8.9533325	-2.1963776	.22851083
-10.097179	3.9950693	-.86550471	.079892979
-6.5108886	2.2828449	-.43019733	.033853067
-8.7806293	3.3035877	-.67443426	.058143163
-4.1503429	1.3608634	-.24120234	.018029097
-3.2115633	.99933672	-.16730636	.011766725
-1.9142931	.54457722	-.082814810	.0052673758
-1.1151402	.29197714	-.040546601	.0023422402
-.59049371	.14356673	-.018324942	.00096628608
-.21586597	.049177841	-.0057429920	.00027306569
-.10874548	.025221598	-.0029086307	.00013446612
-.10874548	.025221598	-.0029086307	.00013446612
-.10874548	.025221598	-.0029086307	.00013446612

Table 2. Results

A	E(eV)	10^{-6} x v(cm/sec)	Q(a.u.)	10^{44}xC$_{app}$(erg cm^4)
5.5	0.2804	0.81987	379.1	2.465
6.0	0.3337	0.89441	370.8	2.599
6.5	0.3916	0.96894	317.8	2.236
6.75	0.4223	1.0062	298.1	2.109
7.25	0.4872	1.0807	296.0	2.242
7.75	0.5567	1.1553	298.0	2.421
8.25	0.6309	1.2298	291.7	2.496
8.5	0.6697	1.2671	284.2	2.472
8.75	0.7097	1.3043	272.1	2.384
9.0	0.7508	1.3416	260.1	2.292
9.5	0.8366	1.4161	239.6	2.139
9.75	0.8812	1.4534	234.0	2.119
10.0	0.9269	1.4907	231.8	2.143
10.5	1.022	1.5652	234.0	2.282
11.5	1.226	1.7143	235.7	2.527
11.75	1.280	1.7515	232.1	2.522
12.0	1.335	1.7888	226.9	2.490
12.5	1.448	1.8633	214.1	2.378
13.0	1.567	1.9379	201.8	2.263
13.5	1.689	2.0124	193.3	2.203
14.0	1.817	2.0869	189.7	2.220
15.0	2.086	2.2360	191.7	2.417
15.5	2.227	2.3105	193.2	2.527
16.0	2.373	2.3851	192.7	2.599
16.5	2.524	2.4596	189.9	2.621
17.0	2.679	2.5341	184.8	2.593
18.0	3.003	2.6832	171.5	2.455
19.0	3.346	2.8323	159.9	2.334
19.5	3.525	2.9068	156.2	2.312
20.0	3.708	2.9814	154.0	2.321
21.0	4.088	3.1304	153.2	2.419
22.0	4.486	3.2795	154.8	2.572
23.0	4.904	3.4286	155.7	2.714
24.0	5.340	3.5776	154.4	2.796
25.0	5.793	3.7269	150.6	2.805
26.0	6.266	3.8758	144.8	2.752
27.0	6.757	4.0248	138.3	2.667
28.0	7.267	4.1739	132.0	2.579
29.0	7.796	4.3230	126.7	2.510
30.0	8.343	4.4720	122.7	2.475
31.0	8.908	4.6211	120.1	2.476
32.0	9.492	4.7702	118.7	2.513
35.0	11.35	5.2174	119.1	2.764
40.0	14.83	5.9627	119.1	3.157
43.0	17.14	6.4099	114.5	3.197
45.0	18.77	6.7080	110.0	3.150
50.0	23.17	7.4534	97.57	2.926
53.0	26.04	7.9006	91.19	2.802
55.0	28.04	8.1987	87.75	2.745
60.0	33.37	8.9441	82.05	2.708
70.0	45.42	10.435	79.35	3.004
80.0	59.32	11.925	80.54	3.511
90.0	75.08	13.416	80.86	3.973
100.0	92.69	14.907	79.26	4.285
110.0	112.2	16.397	76.12	4.435
130.0	156.6	19.379	67.52	4.379
150.0	208.6	22.360	58.43	4.068

LEGEND FOR FIGURES

1. The $HeH^+(\,^1\Sigma^+)$ "best" potential function.

2. Log-log plot of Q vs E (eV), v (cm/sec) and A (a.u.)

3. Ion-atom impact spectrum: extrema of C_{app} vs. $1/v$.
   Below: index N of the extremum vs. $1/v_N$.

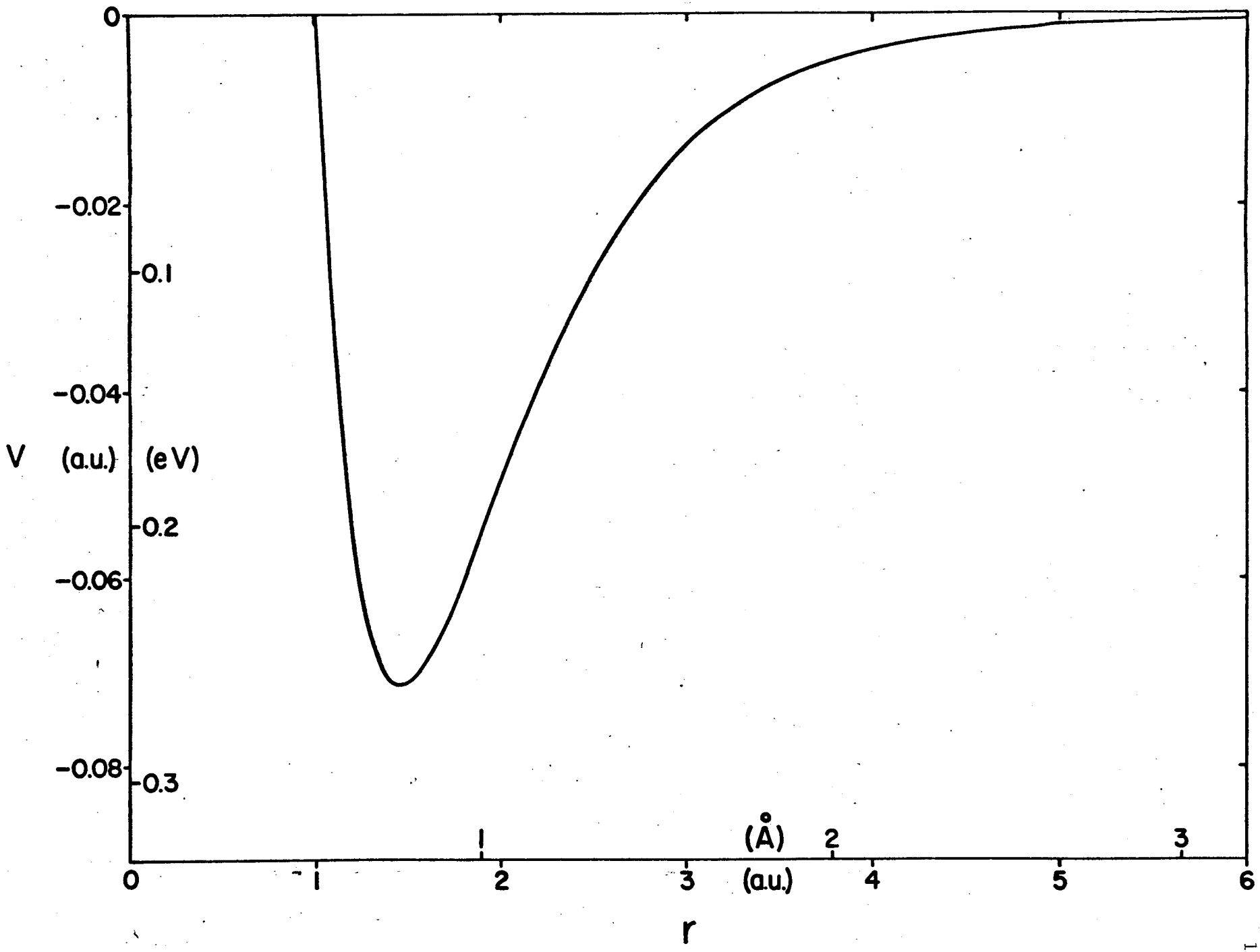


Fig. 1

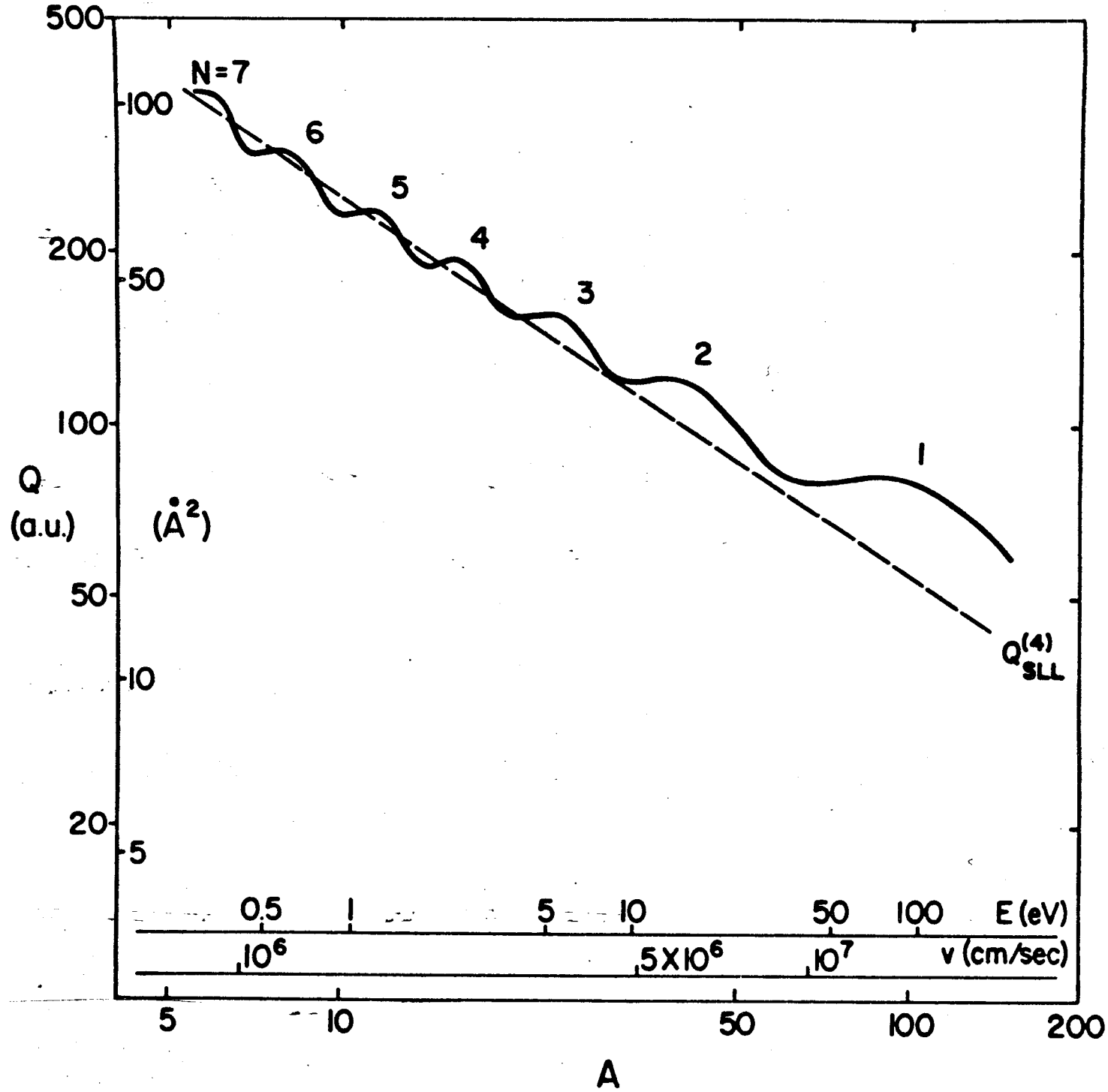
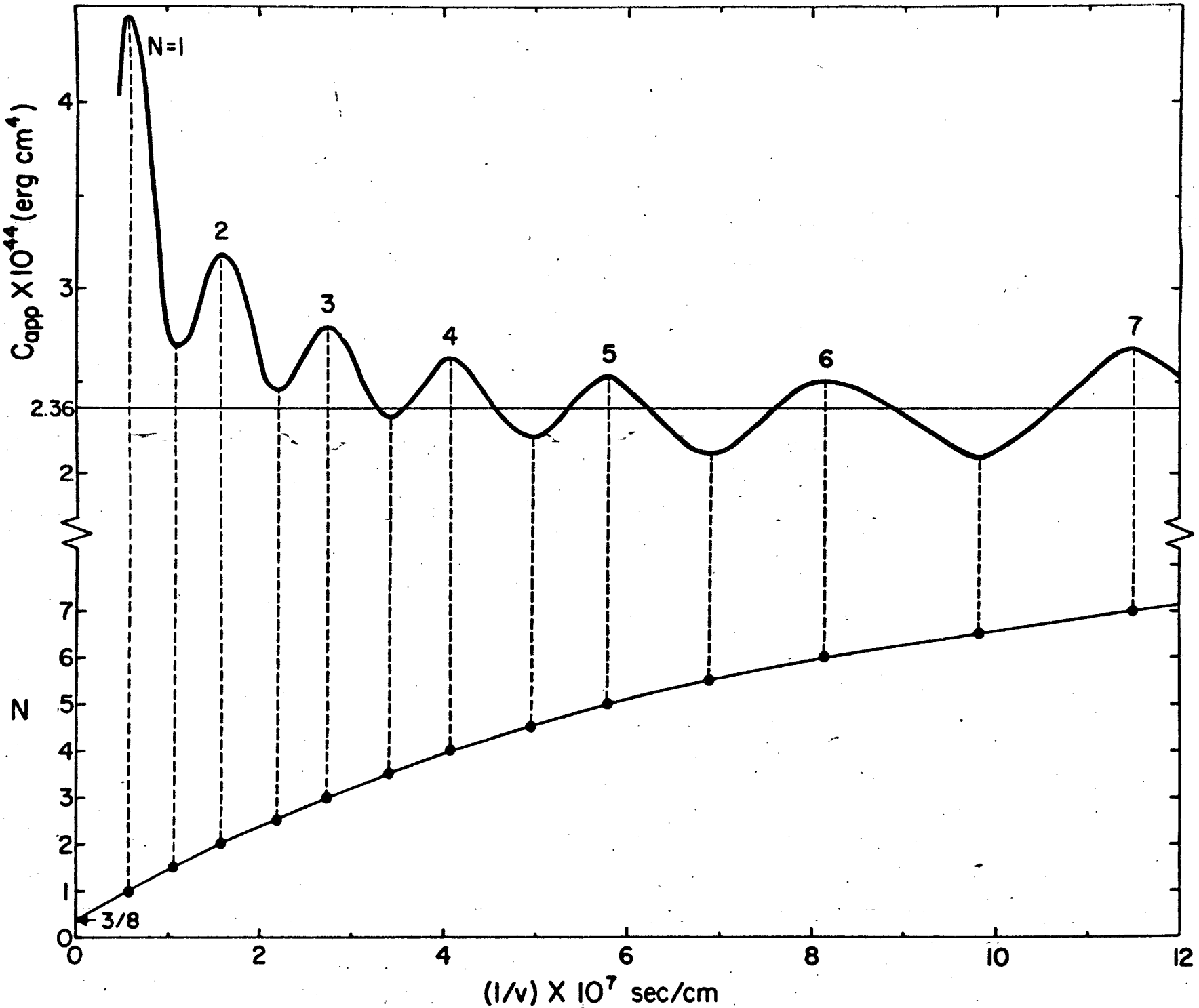

500
200
100
50
20
100
50
10
5
Q
(a.u.)
(Å²)
N=7
6
5
4
3
2
1
$Q^{(4)}_{SLL}$
0.5
1
5
10
50
100
E (eV)
10^6
5×10^6
10^7
v (cm/sec)
5
10
50
100
200
A

Fig. 2


N=1
2
3
4
5
6
7
$C_{app} \times 10^{44}$ (erg cm^4)
4
3
2.36
2
N
7
6
5
4
3
2
1
0
3/8
0
2
4
6
8
10
12
(1/v) X 10^7 sec/cm