Refined Free Electron Model of Porphine and Tetrahydroporphine

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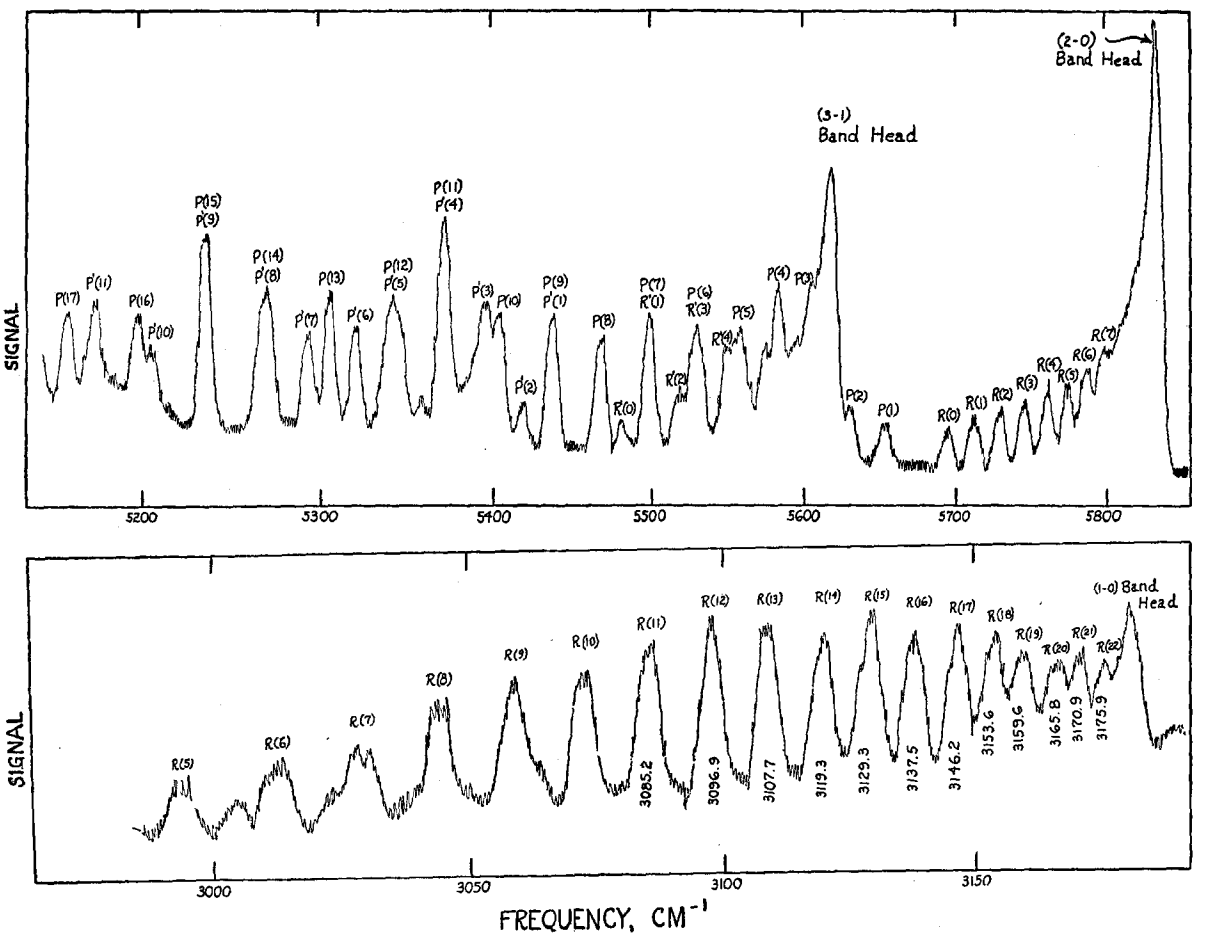

FIG. 1. A portion of the fundamental (lower figure) and first overtone bands (upper figure) of HCl in emission. The traces shown are uncorrected for changes in detector sensitivity. In the upper figure primes refer to the (3–1) transition, unprimed quantities to the (2–0) transition. The numbers in parentheses refer to the J level in the lower state.

maximum at 3063 cm^{-1} (predicted value 3070 cm^{-1}). The weak (4−2) head is probably obscured by overlapping lines.

In the figure we have indicated the frequencies of some of the higher J lines of the (1−0) band. These frequencies are good only to about ± 0.5 cm^{-1}. These new data are, unfortunately, insufficiently accurate to justify a refinement of the formula representing the rotational fine structure. With more regard paid to the design of the flame, higher accuracy could no doubt be obtained and such a refinement could be made.

The pattern of the overtone band is complicated by the superposition of the (2−0) and (3−1) transitions. The individual lines have been assigned as indicated in the figure.

A completely unambiguous estimate of rotational temperature from the data of the (1−0) band has not been made. The peak intensities of the well-resolved lines could not all be fitted to a single temperature parameter. Thus, for example, while the band maximum ($J'=12$ or 13) indicates a $T_{rot} \cong 4500°K$, the intensity distribution of the lines for $J' \geqslant 13$ seem better fitted by a $T_{rot} \cong 2500°K$. The discrepancy is perhaps due to reabsorption by the HCl present in the cooler portions of the flame and in the exhaust gas. If this is the case, then the 2500°K figure is probably the more reliable.

Our estimate of vibrational temperature is also not free from uncertainty. For purposes of calculation it is assumed that (1) the peak intensities of the (2−0) and (3−1) band heads characterize their respective band intensities; (2) the reabsorption at the band heads is small; (3) the ratio of dipole matrix elements M_{31}/M_{20} is equal to $\sqrt{3}$.[6] On this basis $T_{vib} \cong 2500°K$. The agreement of the best estimates of T_{vib} and T_{rot} is probably accidental; however, these figures are not unreasonable in comparison with the maximum temperature attainable from the H_2, Cl_2 reaction, namely ~3000°K.

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Refined Free Electron Model of Porphine and Tetrahydroporphine

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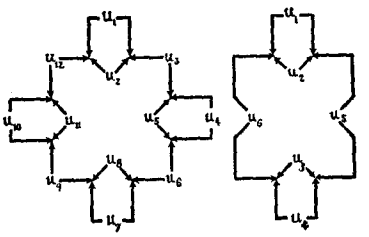
THE electronic structures of porphine and tetrahydroporphine have been studied theoretically by several authors; Longuet-Higgins, Rector, and Platt[1] adopted the simple LCAO MO method and Simpson[2] and Kuhn,[3] the perimeter-free-electron model.

The present writers' calculation is based on a refined free-electron model, which takes into account explicitly the effect of the cross links and hetero-atoms.

The molecular skeleton of porphine is divided into twelve parts (six, in tetrahydroporphine) each of which has its π-electron wave function u_1, u_2, $\cdots$, respectively (Fig. 1). The total one-electron



Porphine Tetrahydroporphine

FIG. 1. Structures of porphine and tetrahydroporphine.

wave functions Ψ's are constructed by connecting u's so as to make Ψ's the bases of the irreducible representations of the symmetry groups D_{4h} (porphine) and D_{2h} (tetrahydroporphine), so that u's must have one of the forms,

$$a\cos\tilde{\omega}x, \quad b\sin\tilde{\omega}x, \quad \text{or} \quad a\cos\tilde{\omega}x+b\sin\tilde{\omega}x.$$

For example, those belonging to the species A_{1u} of D_{4h} are written as

$$u_1=u_4=u_7=u_{10}=b_1\sin\tilde{\omega}x, \quad u_2=u_5=u_8=u_{11}=b_2\sin\tilde{\omega}x,$$
$$u_3=u_6=u_9=u_{12}=b_3\sin\tilde{\omega}x,$$

where x is measured by the one bond length l as a unit, and $\tilde{\omega}$ is related to the orbital energy E by the formula,

$$E=(h^2\tilde{\omega}^2)/(8\pi^2ml^2).$$

Moreover, Ψ's are required to be one-valued and continuous at the point of connection.[4]

These requirements are fulfilled by the following set of relations for the above species:

$$b_1\sin3\tilde{\omega}-b_2\sin2\tilde{\omega}=0,$$
$$b_1\sin3\tilde{\omega}+b_3\sin2\tilde{\omega}=0,$$
$$b_1\cos3\tilde{\omega}+b_2\cos2\tilde{\omega}-b_3\cos2\tilde{\omega}=0,$$

which leads to a determinantal equation,

$$\begin{vmatrix}\sin3\tilde{\omega} & -\sin2\tilde{\omega} & 0\\ \sin3\tilde{\omega} & 0 & \sin2\tilde{\omega}\\ \cos3\tilde{\omega} & \cos2\tilde{\omega} & -\cos2\tilde{\omega}\end{vmatrix}=0.$$

The energy levels are computed by solving this equation for $\tilde{\omega}$. An entirely similar program is followed for the other species. The calculation is calibrated with the "color" of benzene.[2]

The singlet-triplet centers of gravity of several long wavelength transitions thus obtained are shown in Fig. 2 (a), and close agreement with the results of LCAO MO method is found there, except that, in porphine the two transitions $A_{1u}\rightarrow E_g$ and $B_{2u}\rightarrow E_g$ come out on the well-spaced positions and in tetrahydroporphine the transition $B_{1u}\rightarrow B_{3g}$ (24,000 cm^{-1}, $\perp$) is of shorter wavelength than the transition $B_{1u}\rightarrow B_{2g}$ (23,000 cm^{-1}, $\|$) in contrast with the LCAO results where the situations are reversed.

The effect of a nitrogen atom is taken into account by assuming a potential box of a certain length (one or two bond lengths) and depth V in place of the nitrogen atom.

The shift of a transition $\Psi_A\rightarrow\Psi_B$, thus caused, is given as

$$V\left|\int_{-\delta}^{+\delta}(\Psi_B^2-\Psi_A^2)dx\right|$$

by the first-order perturbation theory.

Several choices of the length and depth lead to the results shown in Fig. 2(b), (c).

In tetrahydroporphine the replacement of the two amino-nitrogens by the boxes (one bond length, $V=23{,}000$ cm^{-1}) presents the results considerably different from those of LCAO; the insertion of shallow supplementary boxes ($V'\fallingdotseq0.3$ ev) at the two aza-nitrogens or the extensions of lengths of boxes cause no significant changes. The computed 13,300 cm^{-1}, 16,400

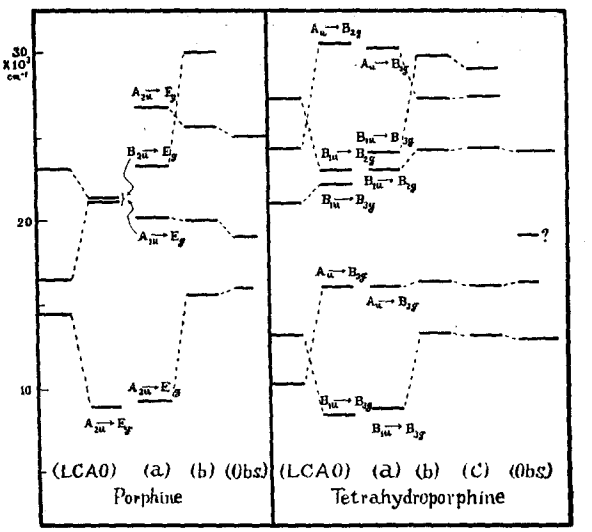


FIG. 2. Comparison of calculated with observed electronic energy states.

Porphine:
(a) $V=0$,
(b) $V=23{,}000$ cm^{-1}, two bond lengths.

Tetrahydroporphine:
(a) $V=0$, $V'=0$,
(b) $V=23{,}000$ cm^{-1}, $V'=0$, one bond length,
(c) $V=21{,}250$ cm^{-1}, $V'=2125$ cm^{-1}, one bond length.

cm^{-1}, and 24,100 cm^{-1} (Soret) transitions agree very well with the observation (Table I) and no transitions are computed near the observed 19,000 cm^{-1} (?) band. In agreement with the conclusion of reference 1, the predicted Soret and 13,000-cm^{-1} bands are polarized $\|$ along, and $\perp$ to, the long axis of the molecule, respectively, and remembering that this molecule is the typical case of the "long-field" spectra,[5] the predicted sequence may be expected to agree well with the observation.

TABLE I. Comparison of calculated centers of gravity with observed singlets.

Molecule	Trans. type	Pol.	Calc[a] (cm^{-1})	Obs (cm^{-1})	LCAO[b] (cm^{-1})
Porphine	$A_{2u}\rightarrow E_g$	$\perp$, $\|$	9300		9000
		Doub. deg	(15,600)	16,000	(14,500)
	$A_{1u}\rightarrow E_g$	$\perp$, $\|$	20,200		21,300
		Doub. deg	(20,200)	19,000	(16,500)
	$A_{2u}\rightarrow E_g$	$\perp$, $\|$	26,800		
		Doub. deg	(25,600)	25,000	
	$B_{2u}\rightarrow E_g$	$\perp$, $\|$	23,300		21,300
		Doub. deg	(30,100)	?	(23,000)
Tetrahydro-porphine	$B_{1u}\rightarrow B_{3g}$	$\perp$	8900 (13,300)	13,000	8700 (13,200)
	$A_u\rightarrow B_{2g}$	$\|$	16,200 (16,400)	16,300 19,000?	16,100 (10,300)
	$B_{1u}\rightarrow B_{2g}$	$\|$	23,000 (24,100)	24,000	23,000 (27,200)
	$B_{1u}\rightarrow B_{3g}$	$\perp$	24,100 (29,700)	?	22,200 (21,000)
	$A_u\rightarrow B_{2g}$	$\perp$	30,300 (27,200)	?	30,400 (24,300)

[a] Predicted energies in brackets are corrected for N atoms.
Potential boxes: Porphine; 2 bond lengths, $V=23{,}000$ cm^{-1}.
Tetrahydroporphine; 1 bond length, $V=23{,}000$ cm^{-1}, $V'=0$.

[b] See reference 1.

In porphine, four nitrogen atoms are assumed equivalent to each other. Although this molecule is one of the representative instances of the "round-field" spectra,[5] where the configuration interaction is supposed to play a more important role than in the former case, the predicted sequence is not so far from the observation, if the potential boxes are extended to two bond lengths and if it is allowed to infer from the experimental absorption curve[6] that the absorption maxima might plausibly exist at 16,000 cm^{-1}, 19,000 cm^{-1} (center of gravity of the bonds 500∼600 mμ) and 25,000 cm^{-1} (Soret).

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The Second Virial Coefficient of a 6–9 Gas at High Temperatures

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THE second virial coefficient[1] of a gas which satisfies a Lennard-Jones 6–9 potential

$$U(r)=\epsilon[2(r_0/r)^9-3(r_0/r)^6] \qquad (1)$$

can be obtained from the expression

$$B(T)=2\pi N\int_0^\infty r^2[1-\exp\{-U(r)/kT\}]dr. \qquad (2)$$

Writing

$$B(T)=(2\pi Nr_0^3/3)G(\theta) \qquad (3)$$

and

$$\theta=\epsilon/kT \qquad (4)$$

it follows[2] that

$$G_9(\theta)=-(2^{1/3}/3)\sum_{n=0}^{\infty}a_n\theta^{(n+1)/3}, \qquad (5)$$

where

$$a_n=\left(\frac{27}{4}\right)^{n/3}\left(\frac{1}{n!}\right)\Gamma\left(\frac{2n-1}{3}\right). \qquad (6)$$

The convergence properties of this series are such that it is difficult to evaluate $G_9(\theta)$ for large values of θ, i.e., at low temperatures. It has been summed, however, for the range $0\leqslant\theta\leqslant 2$ using punched card computing machine techniques such as have previously been employed in determining the corresponding functions for a 6–12 potential.[3a, b] The results are given in Table I. In addition to the function $G_9(\theta)$ itself, the first three derivatives have been computed and tabulated

$$d^iG_9(\theta)/d\theta^i\equiv G_9{}^i(\theta)=-(2^{1/3}/3)\sum_{n=0}^{\infty}a_n{}^i\theta^{(n+1-3i)/3}, \qquad (7)$$

where

$$a_n{}^0\equiv a_n \quad\text{and}\quad G_9{}^0(\theta)\equiv G_9(\theta) \qquad (8)$$

as defined by Eq. (6) and

$$a_n{}^{i+1}=(1/3)(n+1-3i)a_n{}^i \quad\text{for}\quad i\geqslant 0. \qquad (9)$$

All these computations were made by setting up the machines to carry the problem through with ten significant figures, and fifty terms in the series expansions were used. The final data have been rounded off to eight significant figures. These tables have been checked by differencing, out to the fourth differences in all cases, and in some regions to the sixth difference. Analysis of the results shows that the tables are accurate out to the last significant figure given, although it is difficult to conceive of any physical problem where such accuracy would be required. The zeros and turning points of the functions are listed in Table II.

TABLE I. Second virial coefficient and related functions for a 6–9 potential.

θ	G_9 (θ)	$G_9{}'$ (θ)	$G_9{}''$ (θ)	$G_9{}'''$ (θ)
0.01	+0.2603 0942	+4.7755 194	−603.3719 9	+107206.87
0.02	+0.2886 4795	+1.5507 606	−174.3587 4	+15738.812
0.03	+0.2973 9512	+0.3456 5219	−83.5973 82	+5071.0931
0.04	+0.2973 5888	−0.2968 6538	−49.4803 63	+2257.5453
0.05	+0.2922 3662	−0.7002 5286	−32.9325 41	+1200.4922
0.06	+0.2837 6288	−0.9790 9573	−23.6377 92	+714.5414 0
0.07	+0.2728 9656	−1.1846 325	−17.8911 07	+459.7630 4
0.08	+0.2602 2523	−1.3433 167	−14.0886 56	+313.2117 4
0.09	+0.2461 3554	−1.4702 215	−11.4421 83	+222.8904 7
0.10	+0.2308 9562	−1.5745 784	−9.5267 368	+164.1685 1
0.11	+0.2146 9901	−1.6623 633	−8.0964 685	+124.3275 8
0.12	+0.1976 8999	−1.7376 179	−7.0009 865	+96.3386 79
0.13	+0.1799 7889	−1.8031 747	−6.1440 388	+76.0974 05
0.14	+0.1616 5194	−1.8610 785	−5.4616 715	+61.0955 68
0.15	+0.1427 7775	−1.9128 425	−4.9100 300	+49.7406 37
0.16	+0.1234 1172	−1.9596 109	−4.4582 215	+40.9879 04
0.17	+0.1035 9922	−2.0022 648	−4.0839 713	+34.1324 36
0.18	+0.0833 7782	−2.0414 938	−3.7708 891	+28.6867 18
0.19	+0.0627 7893	−2.0778 452	−3.5066 967	+24.3062 15
0.20	+0.0418 2903	−2.1117 593	−3.2820 487	+20.7427 10
0.21	+0.0205 5067	−2.1435 938	−3.0897 306	+17.8142 83
0.22	−0.0010 3690	−2.1736 427	−2.9241 011	+15.3855 25
0.23	−0.0229 1705	−2.2021 498	−2.7806 979	+13.3542 33
0.24	−0.0450 7544	−2.2293 188	−2.6559 540	+11.6422 81
0.25	−0.0674 9955	−2.2553 214	−2.5469 906	+10.1892 56
0.26	−0.0901 7847	−2.2803 034	−2.4514 642	+8.9479 401
0.27	−0.1131 0263	−2.3043 891	−2.3674 512	+7.8810 697
0.28	−0.1362 6362	−2.3276 854	−2.2933 609	+6.9589 707
0.29	−0.1596 5401	−2.3502 849	−2.2278 691	+6.1578 149
0.30	−0.1832 6726	−2.3722 678	−2.1698 661	+5.4583 201
0.31	−0.2070 9755	−2.3937 041	−2.1184 166	+4.8447 698
0.32	−0.2311 3973	−2.4146 553	−2.0727 275	+4.3042 678
0.33	−0.2553 8922	−2.4351 756	−2.0321 234	+3.8261 650
0.34	−0.2798 4196	−2.4553 128	−1.9960 258	+3.4016 163
0.35	−0.3044 9434	−2.4751 094	−1.9639 373	+3.0232 340
0.36	−0.3293 4314	−2.4946 034	−1.9354 281	+2.6848 155
0.37	−0.3543 8551	−2.5138 287	−1.9101 253	+2.3811 275
0.38	−0.3796 1892	−2.5328 156	−1.8877 046	+2.1077 339
0.39	−0.4050 4112	−2.5515 914	−1.8678 823	+1.8608 582
0.40	−0.4306 5013	−2.5701 810	−1.8504 099	+1.6372 714
0.41	−0.4564 4420	−2.5886 067	−1.8350 685	+1.4342 023
0.42	−0.4824 2179	−2.6068 889	−1.8216 654	+1.2492 633
0.43	−0.5085 8156	−2.6250 459	−1.8100 297	+1.0803 900
0.44	−0.5349 2234	−2.6430 948	−1.8000 101	+0.9257 914
0.45	−0.5614 4314	−2.6610 511	−1.7914 716	+0.7839 088
0.46	−0.5881 4310	−2.6789 288	−1.7842 940	+0.6533 810
0.47	−0.6150 2150	−2.6967 411	−1.7783 701	+0.5330 164
0.48	−0.6420 7775	−2.7145 001	−1.7736 033	+0.4217 682
0.49	−0.6693 1136	−2.7322 168	−1.7699 074	+0.3187 150
0.50	−0.6967 2198	−2.7499 015	−1.7672 045	+0.2230 430
0.51	−0.7243 0932	−2.7675 639	−1.7654 243	+0.1340 321
0.52	−0.7520 7321	−2.7852 129	−1.7645 037	+0.0510 435
0.53	−0.7800 1356	−2.8028 567	−1.7643 853	−0.0264 910
0.54	−0.8081 3035	−2.8205 031	−1.7650 171	−0.0990 777
0.55	−0.8364 2365	−2.8381 594	−1.7663 519	−0.1671 689
0.56	−0.8648 9360	−2.8558 323	−1.7683 468	−0.2311 694
0.57	−0.8935 4038	−2.8735 284	−1.7709 628	−0.2914 422
0.58	−0.9223 6426	−2.8912 535	−1.7741 643	−0.3483 133
0.59	−0.9513 6556	−2.9090 135	−1.7779 188	−0.4020 763
0.60	−0.9805 4466	−2.9268 136	−1.7821 964	−0.4529 962
0.61	−1.0099 020	−2.9446 591	−1.7869 700	−0.5013 120
0.62	−1.0394 380	−2.9625 546	−1.7922 147	−0.5472 402
0.63	−1.0691 533	−2.9805 049	−1.7979 075	−0.5909 770
0.64	−1.0990 483	−2.9985 142	−1.8040 275	−0.6327 005
0.65	−1.1291 238	−3.0165 868	−1.8105 553	−0.6725 727
0.66	−1.1593 803	−3.0347 266	−1.8174 733	−0.7107 411
0.67	−1.1898 185	−3.0529 375	−1.8247 649	−0.7473 401
0.68	−1.2204 393	−3.0712 231	−1.8324 153	−0.7824 927
0.69	−1.2512 432	−3.0895 869	−1.8404 103	−0.8163 112
0.70	−1.2822 313	−3.1080 324	−1.8487 374	−0.8488 983
0.71	−1.3134 042	−3.1265 627	−1.8573 845	−0.8803 486
0.72	−1.3447 628	−3.1451 811	−1.8663 408	−0.9107 485
0.73	−1.3763 081	−3.1638 906	−1.8755 963	−0.9401 777
0.74	−1.4080 409	−3.1826 940	−1.8851 414	−0.9687 096
0.75	−1.4399 623	−3.2015 943	−1.8949 677	−0.9964 116
0.76	−1.4720 732	−3.2205 943	−1.9050 671	−1.0233 461
0.77	−1.5043 745	−3.2396 966	−1.9154 322	−1.0495 707
0.78	−1.5368 674	−3.2589 038	−1.9260 563	−1.0751 386
0.79	−1.5695 530	−3.2782 185	−1.9369 330	−1.1000 992
0.80	−1.6024 322	−3.2976 433	−1.9480 564	−1.1244 980
0.81	−1.6355 062	−3.3171 805	−1.9594 212	−1.1483 775
0.82	−1.6687 762	−3.3368 325	−1.9710 224	−1.1717 772
0.83	−1.7022 432	−3.3566 017	−1.9828 553	−1.1947 335
0.84	−1.7359 086	−3.3764 903	−1.9949 157	−1.2172 806
0.85	−1.7697 735	−3.3965 007	−2.0071 996	−1.2394 502
0.86	−1.8038 390	−3.4166 351	−2.0197 035	−1.2612 721
0.87	−1.8381 066	−3.4368 955	−2.0324 240	−1.2827 737
0.88	−1.8725 774	−3.4572 843	−2.0453 580	−1.3039 811
0.89	−1.9072 527	−3.4778 034	−2.0585 027	−1.3249 183
0.90	−1.9421 339	−3.4984 550	−2.0718 556	−1.3456 081
0.91	−1.9772 223	−3.5192 412	−2.0854 141	−1.3660 716
0.92	−2.0125 192	−3.5401 640	−2.0991 763	−1.3863 288
0.93	−2.0480 260	−3.5612 254	−2.1131 401	−1.4063 984
0.94	−2.0837 441	−3.5824 274	−2.1273 037	−1.4262 980
0.95	−2.1196 750	−3.6037 721	−2.1416 655	−1.4460 441
0.96	−2.1558 201	−3.6252 614	−2.1562 241	−1.4656 524
0.97	−2.1921 807	−3.6468 973	−2.1709 782	−1.4851 375
0.98	−2.2287 585	−3.6686 816	−2.1859 265	−1.5045 134
0.99	−2.2655 549	−3.6906 164	−2.2010 681	−1.5237 931
1.00	−2.3025 713	−3.7127 036	−2.2164 021	−1.5429 891
1.05	−2.4910 097	−3.8254 922	−2.2959 341	−1.6381 029
1.10	−2.6851 888	−3.9423 759	−2.3802 031	−1.7326 512
1.15	−2.8853 195	−4.0635 914	−2.4692 064	−1.8276 238
1.20	−3.0916 241	−4.1893 762	−2.5629 859	−1.9238 145
1.25	−3.3043 372	−4.3199 709	−2.6616 191	−2.0218 765
1.30	−3.5237 054	−4.4556 208	−2.7652 139	−2.1223 620
1.35	−3.7499 878	−4.5965 772	−2.8739 037	−2.2257 501
1.40	−3.9834 559	−4.7430 986	−2.9878 444	−2.3324 666
1.45	−4.2243 948	−4.8954 521	−3.1072 124	−2.4429 001
1.50	−4.4731 089	−5.0539 136	−3.2322 025	−2.5574 120
1.55	−4.7298 927	−5.2187 695	−3.3630 273	−2.6763 460
1.60	−4.9950 914	−5.3903 174	−3.4999 163	−2.8000 343
1.65	−5.2690 411	−5.5688 663	−3.6431 154	−2.9288 027
1.70	−5.5521 001	−5.7547 384	−3.7928 866	−3.0629 746
1.75	−5.8446 426	−5.9482 692	−3.9495 083	−3.2028 749
1.80	−6.1470 604	−6.1498 083	−4.1132 750	−3.3488 320
1.85	−6.4597 630	−6.3597 209	−4.2844 980	−3.5011 808
1.90	−6.7831 784	−6.5783 879	−4.4635 054	−3.6602 640
1.95	−7.1177 543	−6.8062 069	−4.6506 425	−3.8264 343
2.00	−7.4639 586	−7.0435 937	−4.8462 730	−4.0000 563

It is of interest to compare the results for a 6–9 potential with those previously derived for a 6–12 potential.[3] From Fig. 1 it is evident that there is a striking similarity in the shape of the two curves. In fact, over a limited temperature range $G_{12}(\theta)$ can be approximated by $AG_9(\alpha\theta)$, where A and α are constants with quite reasonable accuracy. It is this fact which makes it nearly impossible to distinguish between a 6–9 and a 6–12 (or, perhaps, almost any other repulsive power) from second virial coefficient measurements. With a slightly different value of ϵ/k, corresponding to the multiplying factor α, and a simultaneous change in r_0