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Potential Energy Curves for CO*

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Potential energy curves for the $X^1\Sigma^+$, $a^3\Pi_r$, $a'^3\Sigma^+$, $d^3\Delta$, $e^3\Sigma^-$, $A^1\Pi$, and $B^1\Sigma^+$ electronic states of the CO molecule have been calculated by the Rydberg-Klein-Rees method. The curve for the $A^1\Pi$ state will have to bend sharply in the range between 1.9 and 2.1 Å or it will have to pass through a maximum to reach the proper dissociation limit.

INTRODUCTION

THE development and application of various methods for obtaining accurate representations of the potential energy of a diatomic molecule as a function of the internuclear distance has long been an important field of activity.¹ Such curves are significant in their own right as fundamental molecular properties with which results of quantum-mechanical calculations can be compared. Also, any quantitative description of the many phenomena arising from atomic or molecular collisions will ultimately require a detailed knowledge of the interaction energies between the species involved.

Recently, the Rydberg-Klein-Rees (RKR) method² has been used to obtain reliable potential curves for the electronic states of a number of different diatomic

molecules.³ The curves so obtained for NO^{3b} and O₂^{3c} have been useful in formulating possible explanations for the quenching of Hg(³P₁) by NO⁴ and O₂⁵ and for the appearance of the Schumann-Runge bands in flames containing O₂.⁶

Since reliable curves are sometimes quite helpful in any discussion of the mechanisms of chemical reactions, it was felt that a systematic study of the potential curves for various diatomic molecules would be worthwhile. For the moment, we are restricting ourselves to those diatomic species which appear to be present in flames in the hope that a knowledge of the accurate potential curves may lead to a better understanding of the chemistry involved. The present paper deals with CO. The RKR method has been used to obtain potential curves for the $X^1\Sigma^+$, $a^3\Pi_r$, $a'^3\Sigma^+$, $d^3\Delta$, $e^3\Sigma^-$, $A^1\Pi$, and $B^1\Sigma^+$ electronic states.⁷

TABLE I. Potential energy of the $X^1\Sigma^+$ state of CO.^a

v	V (cm ⁻¹)	r_{\max} (Å)	r_{\min} (Å)	V (ev)
0	1082	1.179	1.084	0.1341
1	3225	1.220	1.054	0.3998
2	5342	1.250	1.035	0.6623
3	7432	1.276	1.020	0.9214
4	9496	1.300	1.007	1.1773
5	11533	1.322	0.997	1.4298
6	13544	1.343	0.987	1.6792
7	15530	1.363	0.979	1.9254
8	17488	1.382	0.971	2.1681
9	19425	1.401	0.964	2.4083
10	21332	1.420	0.958	2.6447
11	23215	1.438	0.952	2.8782
12	25073	1.456	0.946	3.1085
13	26904	1.474	0.941	3.3355
14	28708	1.491	0.936	3.5591
15	30487	1.509	0.932	3.7797
16	32240	1.526	0.927	3.9970
17	33967	1.544	0.923	4.2111
18	35665	1.561	0.919	4.4216
19	37342	1.579	0.915	4.6295
20	38996	1.596	0.911	4.8346
21	40623	1.614	0.908	5.0363
22	42207	1.631	0.905	5.2327
23	43778	1.649	0.901	5.4275

^a Experimental data from footnote references 9 and 11-13.

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¹ G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), pp. 101-103.

² (a) R. Rydberg, *Z. Physik* **73**, 376 (1931); (b) O. Klein, *ibid.* **76**, 226 (1932); (c) A. L. G. Rees, *Proc. Phys. Soc. (London)* **A59**, 998 (1947); (d) J. T. Vanderslice, E. A. Mason, W. G. Maisch, and E. R. Lippincott, *J. Mol. Spectroscopy* **3**, 17 (1959).

METHOD AND RESULTS

The RKR method is a WKB procedure for obtaining the classical turning points of the motion directly from the measured vibrational and rotational energy levels of the molecule.² The curves so obtained are thus based directly on the experimental data and therefore should be quite reliable. The method has been amply described in recent articles so the procedure will not be repeated here.^{3,8} The method is rapid and appears to be accurate. Data were obtained from Herzberg and Rao,⁹ Schmid and Gerö,^{10,11} Rao,¹² Pearse and

³ (a) J. T. Vanderslice, E. A. Mason, and E. R. Lippincott, *J. Chem. Phys.* **30**, 129 (1959); (b) J. T. Vanderslice, E. A. Mason, and W. G. Maisch, *ibid.* **31**, 738 (1959); (c) J. T. Vanderslice, E. A. Mason, and W. G. Maisch, *ibid.* **32**, 515 (1960); (d) R. J. Fallon, J. T. Vanderslice, and E. A. Mason, *ibid.* **32**, 698 (1960); (e) R. D. Verma, *ibid.* **32**, 738 (1960).

⁴ R. J. Fallon, J. T. Vanderslice, and E. A. Mason, *J. Phys. Chem.* **63**, 2082 (1959).

⁵ R. J. Fallon, J. T. Vanderslice, and E. A. Mason, *J. Phys. Chem.* **64**, 505 (1960).

⁶ R. J. Fallon, I. Tobias, J. T. Vanderslice, and W. G. Maisch, *Can. J. Chem.* **38**, 743 (1960).

⁷ R. S. Mulliken [*Can. J. Chem.* **36**, 10 (1958)] has pointed out that the state previously labeled ³Π₁ is more than likely a ³Δ.

⁸ F. Gilmore (Rand Corporation, Santa Monica, California) has corrected the basic working equations given in these earlier papers. The numerical results are not significantly affected. See errata published in *J. Mol. Spectroscopy* **5**, 83 (1960) and *J. Chem. Phys.* **33**, 614 (1960).

⁹ G. Herzberg and K. N. Rao, *J. Chem. Phys.* **17**, 1099 (1949).

¹⁰ R. Schmid and L. Gerö, *Z. Physik* **93**, 656 (1935).

¹¹ R. Schmid and L. Gerö, *Z. Physik* **101**, 343 (1936).

¹² K. N. Rao, *Astrophys. J.* **110**, 304 (1949).

TABLE II. Potential energy of the $a^3\Pi_r$ state of CO.^a

v	V (cm ⁻¹)	r_{\max} (Å)	r_{\min} (Å)	V (ev)	$V+T_e$ (ev)
0	866	1.263	1.156	0.1074	6.1431
1	2581	1.310	1.124	0.3200	6.3557
2	4260	1.344	1.103	0.5281	6.5638
3	5925	1.375	1.087	0.7346	6.7703
4	7550	1.403	1.074	0.9360	6.9717
5	9150	1.429	1.063	1.1344	7.1701

^a Experimental data from footnote references 15, 17, and 18.^b T_e is the difference in energy between the bottom of the state in question and the bottom of the $X^1\Sigma^+$ state.TABLE III. Potential energy of the $a'^3\Sigma^+$ state of CO.^a

v	V (cm ⁻¹)	r_{\max} (Å)	r_{\min} (Å)	V (ev)	$V+T_e$ (ev)
0	613	1.423	1.296	0.0759	6.9967
1	1821	1.479	1.257	0.2258	7.1466
2	3009	1.521	1.232	0.3730	7.2938
3	4175	1.558	1.214	0.5176	7.4384
4	5321	1.591	1.198	0.6597	7.5805
5	6447	1.622	1.185	0.7992	7.7200
6	7552	1.652	1.174	0.9363	7.8571
7	8638	1.681	1.164	1.0709	7.9917
8	9704	1.710	1.154	1.2031	8.1239
9	10751	1.737	1.146	1.3329	8.2537
10	11779	1.765	1.139	1.4603	8.3811
11	12788	1.792	1.132	1.5854	8.5062
12	13778	1.819	1.125	1.7082	8.6290
13	14750	1.846	1.119	1.8287	8.7494
14	15703	1.872	1.113	1.9468	8.8676
15	16638	1.899	1.108	2.0627	8.9835
16	17554	1.926	1.103	2.1762	9.0970
17	18451	1.953	1.099	2.2853	9.2083
18	19330	1.981	1.094	2.3965	9.3173
19	20191	2.008	1.090	2.5032	9.4240
20	21033	2.036	1.086	2.6076	9.5283
21	21856	2.064	1.082	2.7096	9.6304
22	22660	2.093	1.078	2.8093	9.7301
23	23445	2.122	1.075	2.9067	9.8274

^a Experimental data from footnote reference 14.TABLE IV. Potential energy of the $d^3\Delta$ state of CO.^a

v	V (cm ⁻¹)	r_{\max} (Å)	r_{\min} (Å)	V (ev)	$V+T_e$ (ev)
0	567	1.448	1.316	0.0703	7.7989
1	1684	1.506	1.277	0.2088	7.9374
2	2792	1.550	1.252	0.3461	8.0747
3	3881	1.589	1.233	0.4812	8.2098
4	4949	1.624	1.217	0.6136	8.3422
5	5998	1.657	1.204	0.7436	8.4722
6	7027	1.688	1.193	0.8712	8.5998
7	8040	1.719	1.183	0.9968	8.7254
8	9035	1.749	1.174	1.1201	8.8487
9	10011	1.778	1.165	1.2411	8.9697
10	10969	1.807	1.158	1.3599	9.0885
11	11899	1.837	1.151	1.4752	9.2038
12	12799	1.868	1.143	1.5868	9.3154
13	13643	1.898	1.137	1.6914	9.4200
14	14506	1.928	1.130	1.7984	9.5270
15	15336	1.959	1.124	1.9013	9.6299
16	16130	1.991	1.119	1.9998	9.7284
17	16911	2.022	1.113	2.0966	9.8252
18	17662	2.054	1.107	2.1897	9.9183
19	18388	2.087	1.102	2.2797	10.0083
20	19094	2.122	1.097	2.3672	10.0958

^a Experimental data from footnote references 15 and 16.TABLE V. Potential energy of the $A^1\Pi$ state of CO.^a

v	V (cm ⁻¹)	r_{\max} (Å)	r_{\min} (Å)	V (ev)	$V+T_e$ (ev)
0	753	1.296	1.182	0.0934	8.1627
1	2229	1.348	1.148	0.2763	8.3456
2	3677	1.387	1.126	0.4559	8.5252
3	5084	1.422	1.110	0.6303	8.6996
4	6462	1.454	1.096	0.8011	8.8704
5	7803	1.484	1.085	0.9674	9.0367
6	9110	1.513	1.075	1.1294	9.1987
7	10394	1.542	1.066	1.2886	9.3579
8	11632	1.571	1.058	1.4421	9.5114
9	12835	1.599	1.050	1.5912	9.6605
10	13998	1.628	1.044	1.7354	9.8047
11	15134	1.656	1.038	1.8763	9.9456
12	16239	1.685	1.032	2.0133	10.0826
13	17309	1.714	1.026	2.1459	10.2152
14	18347	1.744	1.021	2.2746	10.3439
15	19342	1.774	1.017	2.3980	10.4673
16	20305	1.805	1.012	2.5174	10.5867
17	21232	1.836	1.007	2.6323	10.7016
18	22113	1.867	1.003	2.7420	10.8113

^a Experimental data from footnote references 11 and 15.

Gaydon,¹³ Herzberg and Hugo,¹⁴ Tanaka, Jursa, and Le Blanc,¹⁵ Gerö,¹⁶ Budd,¹⁷ and Beer.¹⁸ The results are shown in Tables I-VII and the curves are shown in Fig. 1.

In an earlier paper,^{2d} it was mentioned that, since the RKR method was a WKB procedure, it would be wise to have some check on the magnitude of the higher order terms arising from the WKB method. The only real check was to compare the RKR results with those obtained by the Dunham method,¹⁹ since this procedure

TABLE VI. Potential energy of the $e^3\Sigma^-$ state of CO.^a

v	V (cm ⁻¹)	r_{\max} (Å)	r_{\min} (Å)	V (ev)	$V+T_e$ (ev)
0	545	1.467	1.332	0.0675	8.1659
1	1619	1.527	1.292	0.2008	8.2992
2	2675	1.572	1.266	0.3317	8.4301
3	3712	1.611	1.246	0.4602	8.5586
4	4730	1.647	1.230	0.5864	8.6847
5	5728	1.681	1.217	0.7102	8.8086
6	6708	1.713	1.205	0.8316	8.9300
7	7669	1.745	1.194	0.9507	9.0491
8	8611	1.776	1.185	1.0675	9.1659
9	9534	1.806	1.176	1.1819	9.2803
10	10438	1.836	1.169	1.2940	9.3924
11	11323	1.866	1.161	1.4038	9.5022
12	12190	1.895	1.154	1.5113	9.6096
13	13038	1.924	1.147	1.6164	9.7148
14	13867	1.953	1.140	1.7192	9.8176
15	14678	1.982	1.134	1.8197	9.9181
16	15470	2.012	1.128	1.9179	10.0163
17	16243	2.042	1.124	2.0138	10.1122

^a Experimental data from footnote reference 14.¹³ R. W. B. Pearse and A. J. Gaydon, *Identification of Molecular Spectra* (Chapman and Hall, Ltd., London, 1950).¹⁴ G. Herzberg and T. J. Hugo, *Can. J. Phys.* **33**, 757 (1955).¹⁵ Y. Tanaka, A. S. Jursa, and F. Le Blanc, *J. Chem. Phys.* **26**, 862 (1957).¹⁶ L. Gerö, *Ann. Physik* **35**, 597 (1939).¹⁷ A. Budd, *Z. Physik* **98**, 437 (1936).¹⁸ B. S. Beer, *Z. Physik* **107**, 73 (1937).¹⁹ J. L. Dunham, *Phys. Rev.* **41**, 713, 721 (1932).

TABLE VII. Potential energy of the $B^1\Sigma^+$ state of CO.^a

v	V (cm ⁻¹)	r_{\max} (Å)	r_{\min} (Å)	V (ev)	$V+T_e$ (ev)
0	1065	1.172	1.075	0.1320	10.9110
1	3139	1.215	1.046	0.3892	11.1681
2	5139	1.249	1.027	0.6371	11.4161

^a Experimental data from footnote references 10 and 15.

is known to be accurate near the minimum. Good agreement was obtained. Recently, Jarman^{20,21} has been able to show that the two procedures are equivalent to a first approximation over part of the range of energy. He has expressed the classical turning points of the motion as given by the Rydberg-Klein-Rees procedure in terms of a series expansion involving the vibrational quantum number v . He was able to show that this expansion is the same one that is obtained by inversion of Dunham's series. He then suggests that this series expansion be used to obtain reliable potential curves rapidly. Jarman has published results on the $X^1\Sigma_g^+$ state of N₂ and on the $X^2\Pi_u$ state of OH for levels whose energy is roughly half the dissociation energy. His results agree well with our previously published results^{3a} for N₂ and with our unpublished results on OH.²²

We have not used this method but have preferred to use the original formulation of Rees,^{20,24,8} which is itself rapid. Our reason for doing so is that Jarman's representation cannot be used outside the range of energy levels from which the spectroscopic constants were derived.^{20,21} Also, as v gets larger, the results depend more strongly on $\omega_e z_e$, one of the least reliably known spectroscopic constants, and hence one might expect his procedure to yield results which are not too reliable at the higher v values. Finally, for cases where $\omega_e z_e$ is large, convergence cannot be depended upon.^{20,21}

DISCUSSION

Potential energy curves for the $X^1\Sigma^+$, $a^3\Pi_r$, $a'^3\Sigma^+$, $d^3\Delta$, $e^3\Sigma^-$, $A^1\Pi$, and $B^1\Sigma^+$ states of CO have been calculated by the RKR method. Of the curves obtained, only that of the $A^1\Pi$ state deserves special mention at the moment. Available evidence¹⁵ indicates

²⁰ W. R. Jarman, J. Chem. Phys. **31**, 1137 (1959).

²¹ W. R. Jarman, Can. J. Phys. **38**, 217 (1960).

²² R. J. Fallon, I. Tobias, and J. T. Vanderslice (to be published).

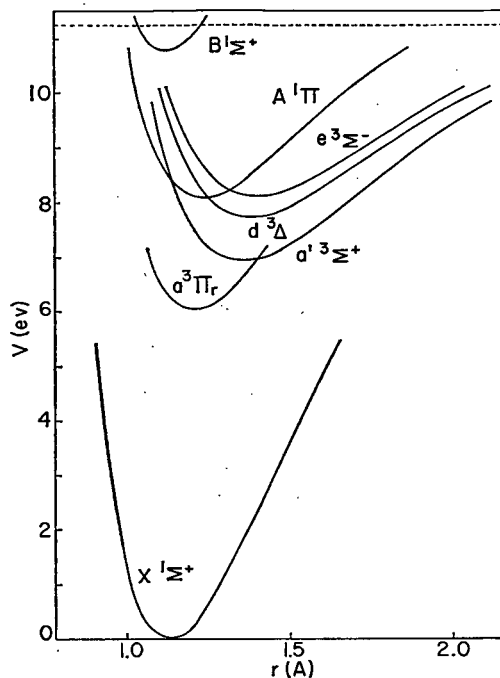


FIG. 1. Potential curves for the different electronic states of CO.

that a molecule in this state dissociates to $C(^3P)$ and $O(^3P)$ corresponding to a dissociation energy D_0 of 11.11 ev. As Fig. 1 shows, the $A^1\Pi$ curve is approaching this limit (dotted line) much more rapidly than those of the three other states, $e^3\Sigma^-$, $d^3\Delta$, and $a'^3\Sigma^+$, which are dissociating to the same limit. This indicates that the curve will either bend over sharply in the region between 1.9 and 2.1 Å or it will show a slight maximum. Mulliken²³ has pointed out that this latter behavior should be more prevalent than is commonly thought. Further experimental and theoretical evidence on this point would be valuable.

Finally, relatively little theoretical work has been done on CO²⁴⁻²⁶ and it will be of interest to see how the extensive calculations now in progress on CO^{27,28} will check with the results reported here.

²³ R. S. Mulliken, J. Phys. Chem. **41**, 5 (1937).

²⁴ W. Moffitt, Proc. Roy. Soc. (London) **A196**, 510, 524 (1949).

²⁵ R. C. Sahni, Trans. Faraday Soc. **49**, 1246 (1953).

²⁶ H. Brion and C. Moser, J. Chem. Phys. **32**, 1194 (1960).

²⁷ P. Merryman, C. M. Moser, and R. K. Nesbet, J. Chem. Phys. **32**, 631 (1960).

²⁸ R. K. Nesbet (private communication).