LETTER TO THE EDITOR

Rydberg-Klein-Rees Potential for the $X^1\Sigma^+$ State of the CO Molecule[1]

The ground electronic state of the CO molecule has become one of the most extensively studied molecular states among diatomic molecules. Since it is a $^1\Sigma$ state, it is free from many of the ambiguities associated with electronic states of higher spin multiplicity and those having nonzero electronic orbital angular momenta. Thus, the ground state of CO can serve as an ideal test case for determining how well a Rydberg–Klein–Rees (1) potential can represent the observed vibrational and rotational energies.

The numerous spectroscopic studies of the CO X $^1\Sigma^+$ state published prior to 1966 have been summarized by Krupenie (2). Until recently, the analysis of the CO A $^1\Pi - X$ $^1\Sigma^+$ Fourth Positive system by Gerö and Schmid (3) was the only basis of the data for $8 \leqq v \leqq 24$. However, advances made during recent years in molecular laser technology have enabled the observation of infrared transitions between high vibrational levels (4). Moreover, accurate spectral positions are now available for vibrational levels through $v = 28$ (5) and it has been shown (6) that these high v value data are consistent with the measurements made by well-established methods for the absorption bands involving $v \leqq 6$. These new laser measurements supplant the earlier electronic data. In addition, the excellent agreement between the grating data (5) for the $P(13)$ line of the 7–6 band (1935.484 cm^{-1}) and the absolute frequency measurement (6) for the same line (58 024 341 MHz or 1935.4834 cm^{-1}; $c = 2.9979250 \times 10^{10}$ cm/sec was used for the conversion from MHz to cm^{-1}) adds additional credence to the calibration techniques (7) employed for determining the spectral positions of the nearly 200 CO laser lines observed in the infrared. These high precision measurements encourage us to apply the Rydberg–Klein–Rees method to the ground electronic state of the CO molecule in order to construct a potential curve to high vibrational levels.

The Rydberg-Klein-Rees method has been a means for determining empirical potential curves for diatomic molecules from experimental data for the vibrational term values $G(v)$ and rotational constants $B(v)$. The theory for this technique is known; essentially, we evaluate the classical turning points $r_{\min}$ $(v, J = 0)$ and $r_{\max}$ $(v, J = 0)$. It can be shown that

$$r_{\max} = (f^2 + f/g)^{1/2} + f \tag{1}$$

$$r_{\min} = (f^2 + f/g)^{1/2} - f, \tag{2}$$

where

$$f = \frac{1}{2}[r_{\max} - r_{\min}] = \frac{\hbar}{(2hc\mu)^{1/2}} \int_{v_{\min}}^{v} \frac{dv'}{[G(v) - G(v')]^{1/2}} \tag{3}$$

TABLE I

RYDBERG-KLEIN-REES POTENTIAL FOR THE $X^1\Sigma^+$ STATE OF THE CO MOLECULE

v	$Y_{00} + G(v)$ [††] (cm^{-1})	r_{min} [**] (Å)		r_{max} [**] (Å)	
		I	II	I	II
0	1081.7778	1.0833255	1.0833250	1.1787905	1.1787898
1	3225.0502	1.0534384	1.0534379	1.2196323	1.2196316
2	5341.8409	1.0342385	1.0342380	1.2499085	1.2499077
3	7432.2173	1.0194122	1.0194117	1.2759352	1.2759345
4	9496.2479	1.0071323	1.0071318	1.2995424	1.2995416
5	11534.0025	0.9965662	0.9965658	1.3215651	1.3215644
6	13545.5522	0.9872522	0.9872518	1.3424683	1.3424675
7	15530.9695	0.9789027	0.9789024	1.3625420	1.3625412
8	17490.3285	0.9713249	0.9713245	1.3819824	1.3819816
9	19423.7047	0.9643817	0.9643814	1.4009294	1.4009285
10	21331.1753	0.9579721	0.9579717	1.4194873	1.4194864
11	23212.8188	0.9520183	0.9520180	1.4377367	1.4377358
12	25068.7152	0.9464610	0.9464607	1.4557413	1.4557405
13	26898.9457	0.9412507	0.9412504	1.4735532	1.4735523
14	28703.5928	0.9363483	0.9363480	1.4912153	1.4912144
15	30482.7399	0.9317213	0.9317210	1.5087639	1.5087630
16	32236.4713	0.9273423	0.9273420	1.5262302	1.5262293
17	33964.8717	0.9231881	0.9231879	1.5436413	1.5436404
18	35668.0262	0.9192390	0.9192388	1.5610213	1.5610203
19	37346.0199	0.9154776	0.9154776	1.5783915	1.5783905
20	38998.9374	0.9118896	0.9118894	1.5957713	1.5957703
21	40626.8630	0.9084613	0.9084610	1.6131785	1.6131775
22	42229.8794	0.9051813	0.9051810	1.6306296	1.6306286
23	43808.0682	0.9020392	0.9020390	1.6481401	1.6481390
24	45361.5087	0.8990259	0.8990257	1.6657243	1.6657233
25	46890.2779	0.8961330	0.8961328	1.6833964	1.6833955
26	48394.4497	0.8933529	0.8933527	1.7011699	1.7011689
27	49874.0946	0.8906789	0.8906787	1.7190577	1.7190567
28	51329.2788	0.8881044	0.8881042	1.7370729	1.7370719

†† $Y_{00} = \dfrac{B_e}{4} + \dfrac{\alpha_e\omega_e}{12B_e} + \dfrac{(\alpha_e\omega_e)^2}{144B_e^3} - \dfrac{\omega_e x_e}{4} = 0.19005 \text{ cm}^{-1}$

$$
\begin{aligned}
G(v) &= \omega_e(v + \tfrac{1}{2}) - \omega_e x_e(v + \tfrac{1}{2})^2 \\
&\quad + \omega_e y_e(v + \tfrac{1}{2})^3 - \omega_e z_e(v + \tfrac{1}{2})^4 \\
&\quad + \omega_e a_e(v + \tfrac{1}{2})^5 - \omega_e b_e(v + \tfrac{1}{2})^6 + \cdots \\
&= 2169.81801(v + \tfrac{1}{2}) - 13.2906899(v + \tfrac{1}{2})^2 + (1.09777979 \times 10^{-2})(v + \tfrac{1}{2})^3 \\
&\quad + (2.29371618 \times 10^{-5})(v + \tfrac{1}{2})^4 + (2.10035541 \times 10^{-6})(v + \tfrac{1}{2})^5 \\
&\quad - (4.49979099 \times 10^{-8})(v + \tfrac{1}{2})^6 + \cdots
\end{aligned}
$$

** See text for discussion of expressions used for calculating columns I & II.

$$
g = \frac{1}{2}\left[\frac{1}{r_{min}} - \frac{1}{r_{max}}\right] = \frac{(2hc\mu)^{1/2}}{\hbar}\int_{v_{min}}^{v}\frac{B(v')dv'}{[G(v) - G(v')]^{1/2}}. \tag{4}
$$

In (3) and (4), lower limit of integration v_{min} is that value of v where $E(v, J = 0) = Y_{00} + G(v)$ vanishes (8); the definition for Y_{00} is given as a footnote to Table I. For the CO $X^1\Sigma^+$ state, the value of v_{min} is -0.50009. The upper limit of integration v causes a singularity

TABLE II

CONSISTENCY TEST OF THE RKR POTENTIAL FOR THE $X\,^1\Sigma^+$ STATE OF THE CO MOLECULE

v	$Y_{00}+G(v)$ (cm^{-1})		$\Delta G(v)$ (cm^{-1})		$B(v)$** (cm^{-1})	
	Spec.[a]	Spec.-Calc.[b]	Spec.[a]	Spec.-Calc.[b]	Spec.[a]	Spec.-Calc.[b]
0	1081.7778	− 9	2143.2724	− 4	1.9225125	+ 9
1	3225.0502	− 13	2116.7907	+ 68	1.9050074	+ 14
2	5341.8409	+ 55	2090.3764	+ 172	1.8875027	+ 33
3	7432.2173	+ 227	2064.0306	+ 2	1.8699983	+ 41
4	9496.2479	+ 229	2037.7546	− 305	1.8524944	− 22
5	11534.0025	− 76	2011.5497	+ 36	1.8349908	− 29
6	13545.5522	− 40	1985.4173	+ 62	1.8174876	+ 68
7	15530.9695	+ 22	1959.3590	− 225	1.7999847	− 23
8	17490.3285	− 203	1933.3763	+ 131	1.7824821	+ 26
9	19423.7047	− 71	1907.4706	− 187	1.7649800	+ 34
10	21331.1753	− 258	1881.6435	+ 62	1.7474782	+ 1
11	23212.8188	− 197	1855.8964	− 134	1.7299767	+ 54
12	25068.7152	− 330	1830.2305	+ 29	1.7124757	+ 9
13	26898.9457	− 301	1804.6471	− 113	1.6949750	+ 51
14	28703.5928	− 415	1779.1471	+ 24	1.6774760	+ 29
15	30482.7399	− 391	1753.7314	− 81	1.6599746	+ 33
16	32236.4713	− 472	1728.4004	+ 14	1.6424750	+ 45
17	33964.8717	− 458	1703.1545	− 8	1.6249757	+ 6
18	35668.0262	− 466	1677.9937	+ 7	1.6074768	+ 30
19	37346.0199	− 458	1652.9176	+ 81	1.5899783	− 21
20	38998.9374	− 377	1627.9255	+ 62	1.5724801	− 37
21	40626.8630	− 315	1603.0164	+ 140	1.5549823	− 63
22	42229.8794	− 176	1578.1888	+ 190	1.5374848	− 136
23	43808.0682	+ 14	1553.4405	+ 208	1.5199877	− 171
24	45361.5087	+ 222	1528.7692	+ 291	1.5024910	− 237
25	46890.2779	+ 513	1504.1719	+ 329	1.4849946	− 322
26	48394.4497	+ 842	1479.6449	+ 339	1.4674986	− 365
27	49874.0946	+ 1181	1455.1842	+ 375	1.4500030	− 414
28	51329.2788	+ 1556			1.4325077	− 439

** $B(v) = B_e - \alpha_e(v + \tfrac{1}{2}) + \gamma_e(v + \tfrac{1}{2})^2 + \cdots$
$= 1.93126515 - (1.75054229 \times 10^{-2})(v + \tfrac{1}{2})$
$+ (1.81117949 \times 10^{-7})(v + \tfrac{1}{2})^2 + \cdots$

[a] The spectroscopic values are given by the expansion coefficients in footnote (††) of Table I and ** above.

[b] The calculated values are obtained by solving the radial wave equation. The (Spec.-Calc.) values are expressed in units of the last digit given in the (Spec.) column.

in the evaluation of these integrals. This numerical problem can be treated by a variety of means. Zeleznik (9) has noted that the singularity may be removed by a change of variable. After integrating Eqs. (3) and (4) by parts, Watson (10) has shown that the functions f and g become

$$f = \frac{\hbar}{(2hc\mu)^{1/2}} \left[\frac{2[G(v) + Y_{00}]^{1/2}}{\omega_e} + 4 \int_{v_{\min}}^{v} \frac{[G(v) - G(v')]^{1/2}}{\omega_{v'}^2} (\omega x)_{v'}\, dv' \right] \quad (5)$$

$$g = \frac{(2hc\mu)^{1/2}}{\hbar} \left[2[G(v) + Y_{00}]^{1/2} \frac{B_e}{\omega_e} + 2 \int_{v_{\min}}^{v} \frac{[G(v) - G(v')]^{1/2}}{\omega_{v'}^2} [2B(v')(\omega x)_{v'} - \alpha_{v'}\omega_{v'}]\, dv' \right], \quad (6)$$

where $\alpha_{v'}$; $\omega v'$; and $(\omega x)_{v'}$ are introduced by means of

$$\frac{dB(v')}{dv'} = -\alpha_{v'} ; \quad \frac{dG(v')}{dv'} = \omega_{v'} ; \quad -\frac{1}{2}\frac{d^2G(v')}{dv'^2} = (\omega x)_{v'} . \tag{7}$$

On the other hand, Albritton, Schmeltekopf, and Zare (11) have evaluated these integrals numerically, where each integral is broken up into a succession of integrals, Simpson's rule is applied up to the region of the singularity, and Gaussian quadrature is used in the region of the singularity.

The computer programs required in both of these alternative formulations are complex. It is of interest and importance to compare the results of these independent evaluations, as is done in Table I. The columns marked I represent the results of Mantz, Watson and Rao obtained by evaluating f and g of Eqs. (5) and (6) and the ones marked II represent the values obtained by Albritton, Schmeltekopf and Zare. Although the difference is systematic, it is less than 0.0000005 Å for $r_{\min}$ and less than 0.0000010 Å for $r_{\max}$; this agreement between the two approaches suggests that both methods yield a reasonably unique RKR potential for the ground electronic state of CO.

The molecular constants actually used in the evaluation of both potentials I and II are given as footnotes to Tables I and II; the number of figures quoted is to avoid round-off errors.

These constants are slightly different from the values quoted in Ref. (5) because, in the determination of the present constants, the $P(11)$ line of the 32–31 band was omitted from the least-squares fit; a more recent examination of the observational data revealed that this particular line was weak and should not be given the same weight as the other lines. Also unlike the previous evaluation, the $\omega_e z_e$ coefficient is statistically determined in the present set. The equilibrium internuclear separation r_e determined from B_e is 1.128341 Å. Although the RKR potential has now been evaluated, there is no *a priori* assurance that this potential represents the actual potential of this molecular state. However, it is possible to discuss critically the consistency of this potential. This has been done by solving the radial wave equation using the RKR potential and examining how well the calculated eigenvalues reproduce the observed energy levels. In addition, vibrational eigenfunctions were employed to compute the expectation value of $h/(8\pi^2\mu r^2 c)$ and hence of $B(v)$. Table II shows the results of these tests where we use the RKR potential labeled II in Table I. The agreement is found to be within the experimental uncertainties of the spectroscopically determined band origins and $B(v)$ values. Thus, we have reason to believe that the RKR potential developed in the present study is close to the true potential of the ground electronic state of the CO molecule.

It may be mentioned that the quality of the agreement between the energy levels would be reduced considerably if Y_{00} is ignored. Secondly, the calculations were, of course, found to be sensitive to the values used for the physical constants. In this investigation, the Planck's constant, the velocity of light and the Avogadro's number given by Taylor, Parker and Langenberg (12) were used in evaluating the turning points. Use of the previously accepted physical constants (13) would introduce changes in the values for the turning points in the sixth decimal place.

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