

Rydberg-Klein-Rees Potential of CO Molecules

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The potential energy curve of CO in X state is calculated using Rydberg-Klein-Rees method. The theoretical background of this method is briefly described. Singular points in integrals are avoided using Watson's method. The output file of the program is also explained.

Theory

Rydberg-Klein-Rees (RKR) method [1] is a procedure to obtain a potential energy curve of diatomic molecules using the rotational- and vibrational energy levels. In contrast to well-known formula such as Morse potential [2], RKR potential has no analytical forms. If you have accurate spectroscopic constants, you can get accurate vibrational-energy level $G(v)$ and rotational constant $B(v)$ and accurate potential curves

In RKR method, classical turning points are calculated by solving

$$f = \frac{1}{2}(r_+ - r_-) = \sqrt{\frac{h}{8\pi^2 c\mu}} \int_{v_{\min}}^v \frac{du}{\sqrt{G(v) - G(u)}} \quad (1)$$

and

$$g = \frac{1}{2}\left(\frac{1}{r_-} - \frac{1}{r_+}\right) = \sqrt{\frac{8\pi^2 c\mu}{h}} \int_{v_{\min}}^v \frac{B(u)du}{\sqrt{G(v) - G(u)}}, \quad (2)$$

where h is the Planck constant, c is the speed of light, μ is the reduced mass, and v_{\min} is a realnumber that satisfies $E(v, J=0) = Y_{00} + G(v) = 0$. From these integrals, we can get

$$r_+ = \left(f^2 + \frac{f}{g}\right)^{1/2} + f \quad (3)$$

and

$$r_- = \left(f^2 + \frac{f}{g}\right)^{1/2} - f \quad (4)$$

The turning points can be calculated using Eqs. (3) and (4). However, the integrals in Eqs. (1) and (2) contains singular points. In order to avoid the singular points, Watson proposed to use the following formula to calculate f and g instead of Eqs. (1) and (2) [2]:

$$f = \sqrt{\frac{h}{8\pi^2 c\mu}} \left\{ \frac{2\sqrt{G(v) + Y_{00}}}{\omega_e} - 2 \int_{v_{\min}}^v \frac{G''(u)\sqrt{G(v) - G(u)}}{(G'(u))^2} du \right\} \quad (5)$$

and

$$g = \sqrt{\frac{8\pi^2 c\mu}{h}} \left\{ \frac{2B_e \sqrt{G(v)} + Y_{00}}{\omega_e} - 2 \int_{v_{\min}}^v \sqrt{G(v) - G(u)} \frac{(B(u)G''(u) - B'(u)G'(u))}{(G'(u))^2} du \right\}. \quad (6)$$

Program output

The attached program calculates the inner and outer turning points using Eqs. (3) - (6). Integrals in Eqs. (5) and (6) are numerically solved using Simpson's method. The output textfile is shown in Fig. 1. The first column is vibrational quantum number. The second column is the vibrational energy level. The third and fourth columns are inner and outer turning points, respectively. The potential energy curve can be plotted using these data and is shown in Fig. 2.

0	1081.777752	1.083239	1.178696
1	3225.050192	1.053354	1.219535
2	5341.840883	1.034156	1.249808
3	7432.217277	1.019331	1.275833
4	9496.247900	1.007052	1.299438
5	11534.002506	0.996486	1.321459
6	13545.552203	0.987173	1.342361
7	15530.969537	0.978824	1.362433
8	17490.328554	0.971247	1.381872
9	19423.704825	0.964305	1.400817
10	21331.175438	0.957895	1.419374
11	23212.818958	0.951942	1.437622
12	25068.715355	0.946385	1.455625
13	26898.945901	0.941175	1.473435
14	28703.593033	0.936273	1.491096
15	30482.740183	0.931647	1.508643
16	32236.471575	0.927268	1.526108
17	33964.871996	0.923114	1.543518
18	35668.026525	0.919165	1.560896
19	37346.020234	0.915405	1.578265
20	38998.937863	0.911817	1.595644
21	40626.863448	0.908389	1.613049
22	42229.879931	0.905109	1.630499
23	43808.068731	0.901967	1.648008
24	45361.509280	0.898954	1.665591
25	46890.278533	0.896061	1.683262
26	48394.450441	0.893281	1.701034
27	49874.095396	0.890608	1.718920
28	51329.279636	0.888033	1.736934

Fig. 1 Output file

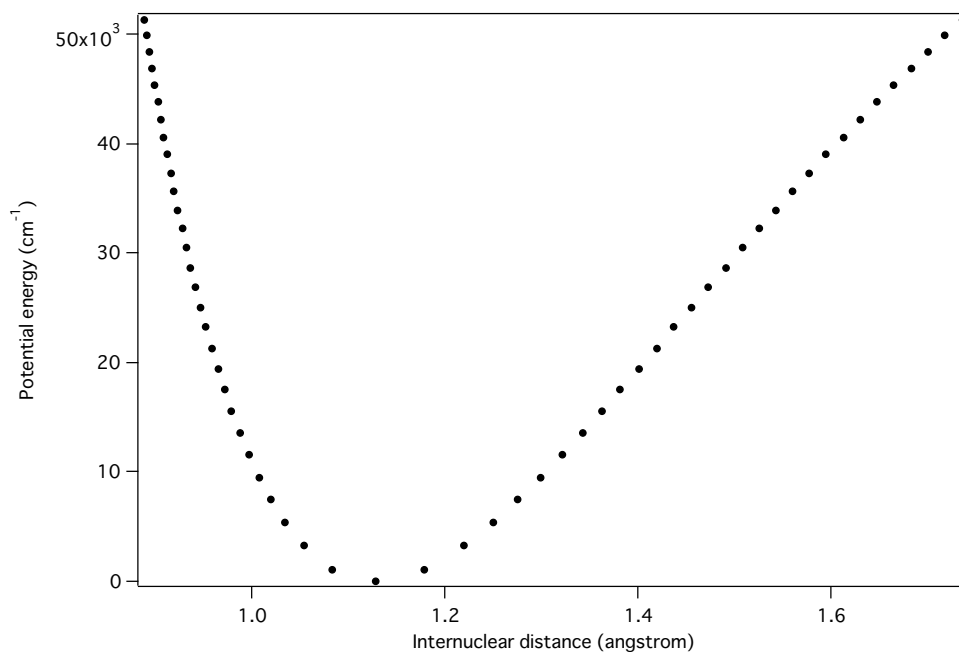


Fig. 2 RKR potential energy curve of CO in X state.

References

- [1] R. Rydberg, *Z. Physik* **73**, 376 (1931) ; O. Klein, *Z. Physik* **76**, 226 (1932) ; A. L. G. Rees, *Proc. Phys. Soc.* **59**, 998(1947)
- [2] A.W.Mantz, J.K.G.Watson, K.N.Rao, D.L.Albritton, A.L.Shmeltekopf, and R.N.Zare, *J.Mol.Spectrosc.* **39**, 180 (1971)