POTENTIAL ENERGY CURVES—A RAPID METHOD

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A rapid method to evaluate the classical turning points for the electronic states of diatomic molecules has been suggested. To check the validity of the present procedure, potential energy curves are constructed for CO and HBr. Our results are in good agreement with the RKR values. In all the cases the agreement is found to be satisfactory with a deviation of 0.1 % to the RKR values.

ОБ ОДНОМ БЫСТРОМ МЕТОДЕ ВЫЧИСЛЕНИЯ КРИВЫХ ПОТЕНЦИАЛЬНОЙ ЭНЕРГИИ

В статье предложен новый быстрый метод для вычисления классических точек поворота в случае электронных состояний двухатомных молекул. С целью проверки обоснованности указанного метода построены кривые потенциальной энергии для CO и HBr. Полученные значения находятся в хорошем согласии со значениями РКР, от которых они во всех рассмотренных случаях отличаются на 0,1 %.

I. INTRODUCTION

The construction of potential energy curves is of considerable importance for the understanding of physical problems arising in astrophysics, gas kinetics and molecular spectra. Also, they permit ready application of the Franck-Condon principle to radiative transitions, dissociation energy and pre-dissociation.

There are numerous methods available in literature [1—15] to construct the true potential energy curves. All these methods involve tedious mathematical calculations. In view of the above Vaidyan and Santaram [16] developed a method for rotationless states, from which one may evaluate the true turning points rapidly with the help of two sets of RKRV turning points.

Table 1

Comparison of the turning points between RKR and the present procedure of HBr and Co

v	$G(v)$ [cm^{-1}]	r_{min} [nm] RKR [21]	r_{min} [nm] Present method	r_{max} [nm] RKR [21]	r_{max} [nm] Present method
		HBr ($X^1\Sigma^+$)			
0	1364.55	0.13115	0.13107	0.15594	0.15407
1	3921.69	0.12479	0.12479	0.16484	0.16495
2	6388.37	0.12092	0.12093	0.17339	0.17343
3	8764.58	0.11804	0.11805	0.18111	0.18109
4	11049.98	0.11573	0.11573	0.18842	0.18835
5	13243.89	0.11387	0.11380	0.19555	0.19542
6	15345.12	0.11219	0.11214	0.20263	0.20243
7	17351.96	0.11077	0.11069	0.20977	0.20944
8	19262.08	0.10953	0.10942	0.21705	0.21654
9	21072.43	0.10843	0.10829	0.22456	0.22378
10	22779.17	0.10744	0.10727	0.23242	0.23121
11	24377.60	0.10656	0.10636	0.24073	0.23888

To simplify the above method, without an appreciable loss in accuracy, a procedure has been suggested to evaluate m and c values without considering the RKR turning points. The present procedure allows to evaluate the true turning points rapidly with a minimum number of spectroscopic constants.

According to Vaidyan and Santaram [16], for

$$r > r_e, \quad \log \left[w_e - (4 w_e x_e U)^{1/2} \right] = m_+ r_{max} + C_+ \text{ and}$$

$$r < r_e, \quad \log \left[w_e + (4 w_e x_e U)^{1/2} \right] = m_- r_{min} + C_- \tag{1}$$

Here, w_e have replaced $\log_{10}$ by $\log_e$ in Eq. (1); i.e. for

$$r > r_e, \quad \ln \left[w_e - (4 w_e x_e U)^{1/2} \right] = m_+ r_{max} + C_+ \text{ and}$$

$$r < r_e, \quad \ln \left[w_e + (4 w_e x_e U)^{1/2} \right] = m_- r_{min} + C_- \tag{2}$$

II. EVALUATION OF THE TURNING POINTS

Table 1. cont.

v	$Y_{00}+C(v)$ [cm^{-1}]	r_{min} [nm] CO(X$^1\Sigma^+$)		r_{max} [nm]	
		RKR [20]	Present method	RKR [20]	Present method
0	1081.77	0.10833	0.10831	0.11787	0.11787
2	5341.84	0.10342	0.10342	0.12499	0.12498
4	9496.24	0.10071	0.10071	0.12995	0.12995
6	13545.55	0.09872	0.09871	0.13424	0.13424
8	17490.32	0.09713	0.09711	0.13819	0.13820
10	21331.17	0.09579	0.09576	0.14194	0.14196
12	25068.71	0.09464	0.09460	0.14557	0.14560
14	28703.59	0.09363	0.09358	0.14912	0.14917
16	32236.47	0.09273	0.09267	0.15262	0.15271
18	35668.02	0.09192	0.09185	0.15610	0.15623
20	38998.93	0.09118	0.09111	0.15957	0.15977
22	42229.87	0.09084	0.09043	0.16306	0.16333
24	45361.50	0.09020	0.08980	0.16657	0.16694
26	48394.14	0.08933	0.08924	0.17012	0.17060
28	51328.85	0.08881	0.08871	0.17371	0.17433
30[2]	54165.98	0.08830	0.08822	0.17733	0.17815
32[2]	56906.01	0.08784	0.08776	0.18103	0.18205
34[2]	59549.40	0.08741	0.08734	0.18482	0.18601
36[2]	62096.53	0.08701	0.08695	0.18869	0.19022

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[1]) These results are available from the authors on request.
[2]) From Ref. [15].

For the 4th and the 3rd vibrational levels, the above eqs. can be written as

$$\ln[w_e \mp (4w_e x_e U_4)^{1/2}] = m_\pm r_{4\pm} + C_\pm \qquad (3)$$

$$\ln[w_e \mp (4w_e x_e U_3)^{1/2}] = m_\pm r_{3\pm} + C_\pm. \qquad (4)$$

In general, for all the molecules, whatever the state may be, few vibrational levels are observed. Here r_3 and r_4 are derived based on the Jarmain method [4]. According to Gilmore [17], the Jarmain method [4] is valid only up to two thirds of the dissociation energy of the state or below ten vibrational levels, as such the 3rd and the 4th vibrational levels are considered in Eqs. (3) and (4). By solving Eqs. (3) and (4) one may obtain the values of $m_\pm$ and $C_\pm$ i.e.,

$$m_\pm = \ln\left[\frac{w_e \pm (4w_e x_e U_4)^{1/2}}{w_e \pm (4w_e x_e U_3)^{1/2}}\right]/(r_4 - r_3). \qquad (5)$$

Here r_4 and r_3 can be derived based on the Jarmain method [4] and the details are given below.
According to the Jarmain method [4],

$$\frac{r}{r_e} = \left[\frac{S_1}{S_1+S_2} + \left(\frac{f}{r_e}\right)^2\right]^{1/2} \pm \frac{f}{r_e}. \qquad (6)$$

By keeping $(w_e x_e/w_e) = K$, $(\alpha_e/B_e) = M$, $(B_e/w_e)^{1/2} = P$ and $V = (v+1/2)$ in the above and neglecting $w_e y_e$, $w_e z_e$, γ_e and other higher powers of K (since K ≪1) in S_1, S_2 and (f/r_e) one can write S_1 and S_2 as follows:

$$S_1 = 1 + \frac{5}{6}KV + \frac{43}{40}K^2V^2 \qquad (7)$$

and

$$S_2 = -\frac{2}{3}MV - \frac{3}{5}KMV^2 - \frac{23}{28}K^2MV^3 \qquad (8)$$

$$\left(\frac{f}{r_e}\right) = 2PV^{1/2} + \frac{10}{6}KPV^{3/2} + \frac{86}{40}K^2PV^{5/2}. \qquad (9)$$

All the spectroscopic constants, e.g. w_e, $w_e x_e$, B_e and α_e are expressed in the units of cm^{-1} and r_e in Å.
Keeping $v = 3$ in $V = (v+1/2)$ in Eqs. (7), (8) and (9), then

$$S_1 + S_2 = h_2\left(1 + \frac{b''}{h_2}K + \frac{c''}{h_2}K^2\right)$$

where $h_2 = 1 - \frac{7}{3}M$, $b'' = 2.9|7 - 7.35 M$, $c'' = 13.169 - 35.219 M$. In Eq. (10) $\left(\frac{b''}{h_2}K + \frac{c''}{h_2}K^2\right) < 1$. Therefore, $(S_1+S_2)^{-1} = \frac{1}{h_2} - \frac{b''}{h_2^2}K + \left(\frac{b''^2}{h_2^3} - \frac{c''}{h_2^2}\right)K^2$. In the above, the higher powers of K are neglected.
Then

$$\left[\frac{S_1}{S_1+S_2} + \left(\frac{f}{r_e}\right)^2\right] = g_2\left(1 + \frac{b_2}{g_2}K + \frac{a_2}{g_2}K^2\right) \qquad (11)$$

where $g_2 = 14P^2 + \frac{1}{h_2}$, $b_2 = \frac{2.917}{h_2} - \frac{b''}{h_2^2} + 81.667P^2$ and

$$a_2 = \frac{b''^2}{h_2^3} - \frac{c''}{h_2^2} - \frac{2.917b''}{h_2^2} + \frac{13.169}{h_2} + 487.822 P^2. \text{ In Eq. (11), } \left(\frac{b_2}{g_2}K + \frac{a_2}{g_2}K^2\right) \text{ is } < 1.$$

Hence

$$\left[\frac{S_1}{S_1+S_2} + \left(\frac{f}{r_e}\right)^2\right]^{1/2} = \sqrt{g_2} + \frac{b_2 K}{2\sqrt{g_2}} + \sqrt{g_2}\left(\frac{a_2}{2g_2} - \frac{b_2^2}{8g_2^2}\right)K^2$$

when compared with $\sqrt{g_2}+b_2K/2\sqrt{g_2}$, K^2 and other higher powers of K are neglected.

$$\cdots\left[\frac{S_1}{S_1+S_2}+\left(\frac{f}{r_e}\right)^2\right]^{1/2}-\sqrt{g_2}+\frac{b_2 K}{2\sqrt{g_2}}$$

$$\frac{r}{r_e}=\left[\frac{S_1}{S_1+S_2}+\left(\frac{f}{r_e}\right)^2\right]^{1/2}=\left(\sqrt{g_2}+\frac{b_2}{2\sqrt{g_2}}K\right)\pm x_3 \qquad (12)$$

x_3 may be obtained by substituting $v=3$ in Eq. (9). Therefore

$$x_3=P(3.74166+10.9132K+49.273K^2). \qquad (13)$$

By proper substitution of Eqs. (12) and (13) in Eq. (6)

$$r_{3\pm}=\left[\frac{b_2}{2\sqrt{g_2}}K+\sqrt{g_2}\pm P(3.74166+10.9132K+49.273K^2)\right]r_e. \qquad (14)$$

Similarly $v=4$ in $V=\left(v+\frac12\right)$ in Eqs. (7), (8) and (9);

$$\left[\frac{S_1}{S_1+S_2}+\left(\frac{f}{r_e}\right)^2\right]^{1/2}\pm\frac{f}{r_e}\quad\text{can be written as follows:}$$

$$\left(\sqrt{g_1}+\frac{b_1}{2\sqrt{g_1}}K\right)\pm x_4 \qquad (15)$$

in which $g_1=\frac{1}{h_1}+18P^2$, $b_1=\frac{3.750}{h_1}-\frac{b'}{h_1^2}+135P^2$

where $h_1=1-3M$, $b'=3.75-12.15M$ and

$$x_4=P(4.24264+15.9099K+92.357K^2). \qquad (16)$$

Then,

$$r_{4\pm}=\left[\frac{b_1K}{2\sqrt{g_1}}+\sqrt{g_1}\pm P(4.24264+15.9099K+92.357K^2)\right]r_e. \qquad (17)$$

From Eqs. (17) and (14) we have for

$$r_{\pm},(r_4-r_3)=\left[\left\{\frac{b_1}{2\sqrt{g_1}}-\frac{b_2}{2\sqrt{g_2}}\right\}K+(\sqrt{g_1}-\sqrt{g_2})\pm(x_4-x_3)\right]r_e. \qquad (18)$$

From Eqs. (13) and (16)

$$(x_4-x_3)=P(0.501+4.997K+43.084K^2).$$

Eq. (18) is used in Eq. (5) to evaluate $m_\pm$.

The obtained $m_\pm$ and $r_{3\pm}$ values are then substituted in the following relations.

$$\text{For } r>r_e,\ \ln[w_e-(4w_ex_eU_3)^{1/2}]=m_+r_{3+}+C_+ \qquad (19)$$

$$\text{for, } r<r_e,\ \ln[w_e+(4w_ex_eU_4)^{1/2}]=m_+r_{3-}+C_- \qquad (20)$$

to evaluate $C_\pm$ values.

Knowing the values $m_\pm$ from Eq. (5) and $C_\pm$ from Eqs. (19) and (20), one can evaluate the turning points rapidly by varying the ,,U'' values in Eq. (2).

The molecular constants required for the present work have been taken from Huber and Herzberg [18] and Bernage and Niay [19].

III. RESULTS AND DISCUSSION

The evaluated turning points are in good agreement with the RKRV values [20, 21]. The modified Vaidyan and Santaram method of the authors') has been successfully verified for a number of molecules such as N_2, OH, OH^+, NaH, RbH, KH, SO^+, SF and CrO.

Our results are in better agreement with the values obtained from the RKRV and the RKR methods than those of Sandeman [14] and Gogawale et al. [22]. A slight difference has been observed in agreement with the RKRV values for higher vibrational levels. The main advantage of the present method compared with the Vaidyan and Santaram method [16] is that one may evaluate the turning points without considering the RKRV values.

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