

A new approximation method to obtain vibration eigenfunctions suitable for a new oscillator model

B S NAVATI and V M KORWAR

Department of Physics, Karnatak University, Dharwad 580 003, India

MS received 9 August 1982; revised 21 April 1983

Abstract. A new oscillator model has been proposed by introducing some modifications in the Morse potential function. Its efficacy is tested by taking a number of electronic states of diatomic molecules. For comparison the Hulbert-Hirschfelder model potential is also used. A new approximation method to find the vibrational eigenfunctions suitable for the new oscillator model has been reported. Langer's method has been used to determine the wavefunctions. Franck-Condon factors and r -centroids are reported for the observed bands of $D^1\Pi - X^1\Sigma$ system of SnO molecule.

Keywords. New oscillator model; new approximation method; vibration eigen function; Franck-Condon factor; r -centroids.

1. Introduction

Intensity distribution in molecular band system forms an important aspect of electronic spectra. Knowledge of vibration transition probabilities is required to explain the intensity distribution in a molecular band system. To a good approximation Franck-Condon factors are proportional to these transition probabilities. One of the most important quantities that enters the Schrödinger wave equation is the potential function. Numerous potential functions have been proposed by various investigators. A thorough review of the potential functions has been made by Varshni (1957) and Steele *et al* (1962). The Schrödinger wave equation is solvable exactly only for a few potential functions such as Morse (1929) and Tietz (1970). A number of approximation methods are also available in literature to solve the wave equation. It is customary in the determination of Franck-Condon (FC) factors to use the Morse oscillator model. But this oscillator model is found unsuitable for a number of electronic states of many diatomic molecules. Theoreticians propose new oscillator models to achieve better agreement between experiment and theory. In the present investigation one such new oscillator model has been proposed for diatomic molecules, and its efficacy is tested for $D^2\Sigma$ AlO, $B^2\Sigma$ LaO, $X^1\Sigma$ SiO, $X^1\Sigma$ GeO, $X^1\Sigma$ SnO, and $D^1\Pi$ SnO electronic states. The Hulbert-Hirschfelder (1941) model potential has been processed with a view to comparing the results with those of the Morse-Korwar-Navati model (hereafter abbreviated as MKN model). A new approximation method has been evolved to solve the one-dimensional time-independent Schrödinger wave equation with the new oscillator model. Applicability of this method has been tested by considering the $D^1\Pi - X^1\Sigma$ transition of SnO molecule. Results of the

application of this method are compared with the results obtained by Langer's method and realistic Rydberg-Klein-Rees (RKR) method.

2. A new oscillator model

2.1 MKN Oscillator model

Mathematically, the simple Morse potential function

$$U_1 = D_e [1 - \exp \{-\alpha (r - r_e)\}]^2, \quad (1)$$

uses only three spectroscopic constants, hence its flexibility is limited. In order to increase the flexibility of the parameter α of the Morse function, it is proposed to consider α as a function of internuclear distance. The modified Morse function will then have the form

$$U_2 = D_e [1 - \exp \{-\alpha(r) (r - r_e)\}]^2. \quad (2)$$

To arrive at the nature and form of the function $\alpha(r)$, an empirical method was adopted. The ultimate form of the function satisfied all the necessary conditions that a conventional potential function has to satisfy. The simple Morse function as in equation (1) was fitted to the realistic RKR turning points of each of the vibrational levels right from $v=0$ to $v=10$ of the $D^2\Sigma A10$ electronic state. Values of $\alpha(r_{\min})$ and $\alpha(r_{\max})$ were determined. Then the graph of $\ln \alpha(r)$ against $(r_e/r - 1)$ was plotted. The nature of the distribution of the points on the graph suggested the following form for $\alpha(r)$

$$\ln \alpha(r) = b \{(r_e/r)^2 - 1\} + a \{(r_e/r) - 1\} + \ln a. \quad (3)$$

Therefore, the ultimate form of $\alpha(r)$ evolved to

$$\alpha(r) = a \exp \left[b \left\{ \left(\frac{r_e}{r} \right)^2 - 1 \right\} + a \left\{ \frac{r_e}{r} - 1 \right\} \right]. \quad (4)$$

The modified Morse function, which we refer to as MKN, assumes the form (2) with $\alpha(r)$ as defined in (4). The MKN model potential function satisfies the usual conditions to be satisfied by potential functions at $r = \infty$ and $r = r_e$. The internuclear distance never assumes the value equal to zero, therefore condition $U(r=0) = \infty$ need not be strictly satisfied; nevertheless the conventional form demands that at $r \ll r_d$ the potential function value must be extremely large; here r_d is the value of r_{\min} for which $U(r_{\min} = r_d) = D_e$. With $\alpha(r)$ as in (4) the model potential becomes more flexible and the results of potential function become remarkably good. Therefore, the above choice of $\alpha(r)$ is suitable and justifiable.

2.2 Determination of constants of MKN function

By fitting the MKN function to the conditions

$$U(r = \infty) = D_e, \quad (5)$$

$$(dU/dr)_{r=r_e} = 0, \quad (6)$$

$$(d^2U/dr^2)_{r=r_e} = K_e, \quad (7)$$

$$(d^3U/dr^3)_{r=r_e} = \text{factor that determines higher order constant}, \quad (8)$$

$$(d^4U/dr^4)_{r=r_e} = \text{factor that determines higher order constant}, \quad (9)$$

and also by expanding the modified Morse function in the form of power series function of Dunham (1932) and comparing the coefficients of this expansion with the Dunham coefficients we obtain the following expressions which determine the constants of MKN function.

$$a = [K_e/2D_e]^{1/2}; \quad p = a + 2b \quad (10)$$

$$w_e a_e/6B_e^2 = \Delta^{(1/2)} - 1 - 2p, \quad (11)$$

$$\mu_A r_e^2 w_e x_e/W = 8\Delta + 24p [\Delta^{(1/2)} - 1] - 24b + 36p^2 \quad (12)$$

$$\Delta = K_e r_e^2/2D_e \quad (13)$$

$$W = (64\pi^2 c \mu_A \times 1.6597 \times 10^{-24})/h \quad (14)$$

$$= 2.1083089 \times 10^{-16} \text{ with the latest values of } c \text{ and } h.$$

In all the above equations quantities such as w_e , $w_e x_e$, D_e , B_e , and a_e are in cm^{-1} units and reduced mass μ_A is in amu. The background necessary to arrive at these equations is given in Varshni (1957).

2.3 Results

Vibrational constants employed in the present investigation are taken from Tawde *et al* (1972) and Murthy and Murthy (1970) for $D^2\Sigma$ AlO and $B^2\Sigma$ LaO states respectively. Constants reported in Herzberg (1950) are used for $X^1\Sigma$ SiO and $X^1\Sigma$ GeO. For spectroscopic constants of $X^1\Sigma$ SnO and $D^1\Pi$ SnO states, the values of Patil (1978) has been referred to. The results using MKN function for the electronic states mentioned earlier are reported in tables 1, 2a and 2b. The Hulbert-Hirschfelder (1941) (H-H) model potential results are also incorporated in tables 2a and 2b.

Table 1. Turning points (Å).

r_{\min}				r_{\max}		
RKR	MKN	Morse	V	RKR	MKN	Morse
1·6619 (1·801)	1·6620 1·8007	1·6621 (1·800)	0	1·7902 (1·915)	1·7902 1·9141	1·7904 (1·914)
1·6218 (1·764)	1·6221 1·7638	1·6221 (1·763)	1	1·8454 (1·961)	1·8455 1·9606	1·8458 (1·959)
1·5960 (1·740)	1·5962 1·7398	1·5965 (1·738)	2	1·8865 (1·995)	1·8863 1·9944	1·8871 (1·992)
1·5760 (1·722)	1·5763 1·721	1·5768 (1·718)	3	1·9219 (2·023)	1·9217 2·0228	1·9227 (2·020)
1·5595 (1·706)	1·5598 1·7053	1·5605 (1·702)	4	1·9541 (2·049)	1·9539 2·0483	1·9551 (2·045)
1·5455 (1·692)	1·5456 1·6917	1·5465 (1·687)	5	1·9845 (2·072)	1·9841 2·0716	1·9855 (2·067)
1·5326 (1·680)	1·5331 1·6796	1·5342 (1·674)	6	2·0129 (2·094)	2·0128 2·0936	2·0145 (2·089)
1·5212 (1·669)	1·5219 1·6686	1·5231 (1·663)	7	2·0405 (2·115)	2·0406 2·1143	2·0423 (2·109)
1·5109 (1·660)	1·5118 1·6586	1·5131 (1·652)	8	2·0673 (2·139)	2·0675 2·1341	2·0693 (2·128)
1·5014 (1·650)	1·5025 1·6495	1·5040 (1·642)	9	2·0936 (2·154)	2·0939 2·1531	2·0962 (2·146)
1·4926 (1·642)	1·4939 1·6410	1·4956 (1·633)	10	2·1193 (2·173)	2·1199 2·1713	2·1223 (2·164)

The first line data of RKR & Morse functions are for $A10 D^2\Sigma$ state (Tulasigeri 1972).
Bracketed data corresponding to $B^2\Sigma$ LaO are Murthy's (1970).

Table 2a. Vibrational energies (cm^{-1}).

U (obs)	Present work		V	Present work		U (obs)
	$U(r_{\min})$	$U(r_{\max})$		$U(r_{\min})$	$U(r_{\max})$	
	$X^1\Sigma$ GeO			$X^1\Sigma$ SiO		
491·7	493·94 493·87	492·24 492·15	0	621·04 620·90	618·55 618·44	619·5
1465·7	1472·26 1471·96	1468·79 1468·64	1	1851·82 1851·44	1845·09 1844·74	1848·5
2434·5	2440·87 2440·25	2436·76 2436·73	2	3071·93 3071·15	3063·73 3063·43	3067·5
3395·2	3401·26 3400·27	3393·68 3393·78	3	4285·79 4284·69	4269·71 4269·31	4273·5
4347·8	4349·66 4347·82	4344·36 4344·77	4	5478·89 5477·26	5461·01 5462·26	5465·5
5292·6	5301·13 5298·69	5298·50 5290·46	5	6666·93 6664·69	6641·75 6641·58	6648·5
6224·6	6233·16 6229·42	6220·61 6222·18	6	7840·77 7837·58	7806·55 7806·76	7817·5
7151·6	7160·35 7155·54	7145·55 7148·12	7	9010·23 9005·97	8967·64 8968·17	8974·5
8071·6	8072·60 8066·31	8064·43 8068·06	8	10161·43 10156·42	10107·25 10108·23	10118·5
8979·6	8986·29 8978·20	8964·98 8969·85	9	11301·13 11294·74	11239·40 11241·06	11252·5
9879·6	9889·76 9879·58	9866·03 9870·67	10	12442·73 12434·86	12357·62 12360·12	12372·5

Upper values correspond to MKN potential and lower values are due to (H-H) potential.

Table 2b. Vibrational energies (cm⁻¹).

U (obs)	Present work		V	Present work		U (obs)
	U (r _{min})	U (r _{max})		U (r _{min})	U (r _{max})	
	X ¹ Σ SnO			D ¹ Π SnO		
410·12	402·15	417·17	0	288·90	285·19	289·23
	402·09	417·12		288·64	284·95	
1224·75	1208·47	1237·65	1	859·89	853·25	863·07
	1208·18	1237·46		858·98	852·67	
2031·94	2014·24	2045·39	2	1422·76	1416·04	1430·75
	2013·52	2045·06		1420·97	1415·98	
2831·66	2810·50	2847·05	3	1978·56	1974·51	1992·27
	2809·13	2846·58		1975·57	1974·05	
3623·92	3599·73	3640·85	4	2528·21	2526·21	2547·63
	3597·50	3640·29		2523·69	2526·31	
4408·72	4383·13	4426·39	5	3070·30	3072·54	3096·83
	4379·80	4425·75		3063·88	3073·56	
5186·06	5158·69	5204·72	6	3604·94	3613·35	3639·87
	5154·02	5204·07		3596·23	3615·68	
5955·94	5927·86	5975·12	7	4134·41	4148·12	4176·75
	5921·60	5974·53		4121·61	4152·19	
6718·36	6689·97	6737·98	8	4653·59	4677·42	4707·47
	6681·88	6737·52		4639·09	4683·52	
7473·32	7445·98	7492·97	9	5167·07	5200·86	5232·63
	7435·79	7492·71		5149·08	5209·42	
8220·82	8195·27	8240·23	10	5672·92	5718·68	5750·43
	8182·75	8240·38		5651·03	5730·07	

Upper values correspond to MKN potential and lower values are that of (H-H) potential.

3. A new approximation method to find eigenfunctions

The solution of one-dimensional time-independent Schrödinger wave equation with Morse oscillator model as in (1) is well known. The un-normalized wave functions suitable for the Morse-oscillator model are of the form,

$$\Phi_1^v(Z) = \exp(-Z/2) Z^{\frac{1}{2}(K-2v-1)} \frac{\mathcal{L}_{K-2v-1}^v(Z)}{K-v-1} \tag{15}$$

where $Z = K \exp\{-a(r-r_e)\}$; $K = w_e/w_e x_e$ (16)

$$\frac{\mathcal{L}_{K-2v-1}^v(Z)}{K-v-1} = (-1)^v \sum_{l=0}^v (-1)^l \binom{v}{l} \frac{\Gamma(K-v)}{\Gamma(K-v-l)} Z^{v-l} \tag{17}$$

In the case of MKN oscillator model let the function $\alpha(r)$ take the values $\alpha_1, \alpha_2, \alpha_3, \alpha_4, \dots, \alpha_j, \dots$ for internuclear distances $r_1, r_2, r_3, r_4, \dots, r_j, \dots$ respectively. Taking each value of α as constant we can construct one Morse oscillator. Let these new types of Morse oscillator potentials be $U_{11}, U_{12}, U_{13}, U_{14}, \dots, U_{1j}, \dots$ with the above values of α respectively. Then we can have as many Morse oscillator potentials as there are $\alpha(r)$ values. This new type of Morse oscillator potential with $\alpha(r=r_j)=\alpha_j=\text{constant}$, will have the form

$$U_{1j} = D_e [1 - \exp \{-\alpha_j (r - r_e)\}]^2. \quad (18)$$

The function $\alpha(r)$ of the MKN potential function varies very slowly in all the regions of r , hence U_{1j} will be very nearly equal to U_2 on either side of the internuclear distance $r = r_j$. That is,

$$\begin{aligned} |U_{1j} - U_2| &= 0 \text{ at } r = r_j, \\ &\approx 0 \text{ at } r \gtrsim r_j \text{ but near } r_j, \end{aligned} \quad (19)$$

Therefore, the solutions of the Schrödinger wave equations

$$\frac{d^2 \Psi_{1j}^v}{dr^2} + \frac{2\mu}{\hbar^2} [E - U_{1j}] \Psi_{1j}^v = 0 \text{ and,} \quad (20)$$

$$\frac{d^2 \Psi_2^v}{dr^2} + \frac{2\mu}{\hbar^2} [E - U_2] \Psi_2^v = 0, \quad (21)$$

at internuclear distance $r = r_j$ must be equal to each other approximately viz

$$\Psi_{1j}^v (r = r_j) \approx \Psi_2^v (r = r_j) \quad (22)$$

The approximate equality as in (22) follows from the fact that at the internuclear distance $r = r_j$ the conditions (19) and an additional condition

$$(\frac{d^2 \Psi_{1j}^v}{dr^2})_{r=r_j} \approx (\frac{d^2 \Psi_2^v}{dr^2})_{r=r_j}. \quad (23)$$

hold good reasonably. With this good approximation we can now get the values of the un-normalized wavefunctions suitable for MKN function at $r = r_j$ as

$$\Phi_2^v (r = r_j) = \Phi_{1j}^v (r = r_j). \quad (24)$$

Since U_{1j} has the form of the Morse oscillator model the solutions must also be the Morse oscillator model solutions. The exact un-normalized solutions of one-dimensional Schrödinger equation with U_{1j} as the Morse oscillator are Φ_{1j}^v . This Φ_{1j}^v must have the form as in (15), (16) and (17) with the value of α replaced by α_j . Therefore, the value of Φ_{1j}^v at $r = r_j$ is as given below.

$$\Phi_{1j}^v(r=r_j) = \exp(-Z_j/2) Z_j^{\frac{1}{2}(K-2v-1)} \frac{\mathcal{L}_{K-v-1}^{(Z_j)}}{K-v-1} \quad (25)$$

$$\text{where } Z_j = K \exp\{-a_j(r_j - r_e)\}, \quad (26)$$

$$K = w_e/w_e x_e, \quad (27)$$

$$\frac{\mathcal{L}_{K-2v-1}^{(Z_j)}}{K-v-1} = (-1)^v \sum_{l=0}^v (-1)^l \binom{v}{l} \frac{\Gamma(K-v)}{\Gamma(K-v-l)} Z_j^{v-l} \quad (28)$$

the associated Laguerre polynomials. For chosen value of r_j the value of a_j is determined taking (4) and then relations (25) to (28) are used to calculate the un-normalized wavefunction value at that chosen value of r_j .

In the present work, the value of the un-normalized wave functions (for a given vibrational quantum number) is computed for each internuclear distance at the intervals of 0.01 Å. Numerical integration method was adopted to determine the normalizing constant N_v . The normalization condition is given by

$$N_v^2 \int \Phi_2^{*v} \Phi_2^v dr = 1, \quad (29)$$

where $\Psi_2^v = N_v \Phi_2^v =$ Normalized wavefunctions suitable for MKN potential.

4. Calculation of Franck-Condon factors

For vibrational quantum numbers up to $v=6$ of $X^1\Sigma$ and up to $v=2$ of $D^1\Pi$ electronic states of SnO molecule, normalized eigenfunctions are obtained by using the method proposed in § 3. These values agree fairly well with the RKR values of Patil and Korwar (1978) and the agreement is much better than for values obtained using the method of Langer (1949). Langer's method was also applied to this new potential to obtain eigenfunctions at low quantum numbers. Tables 3a and 3b list the wavefunctions for $v''=1$ and $v'=1$ of $X^1\Sigma$ and $D^1\Pi$ of SnO respectively. For comparison eigenfunctions Ψ_{MKN} and Ψ_{RKR} are also given. The results are reasonably good. Overlap integrals were computed using numerical integration. Results have been reported in table 4 along with the RKR and Morse results of Patil and Korwar (1978).

5. r -Centroids

The r -centroids are defined as

$$\bar{r}_{v'v''} = \frac{\int \Psi^{*v'} r \Psi^{v''} dr}{\int \Psi^{*v'} \Psi^{v''} dr}. \quad (31)$$

Table 3a. SnO ($X^1\Sigma$) eigenfunction $v' = 1$.

Inter-nuclear distance r	RKR (DCP)	MKN New Approximation	MKN Langer (1949)	Inter-nuclear distance r	RKR (DCP)	MKN New Approximation	MKN Langer (1949)
2.09	—	0.001890	0.001802	1.86	1.737	1.756914	1.760079
2.08	—	0.003562	0.003415	1.85	1.034	1.048709	1.043929
2.07	0.006	0.006556	0.006321	1.84	0.233	0.238209	0.226248
2.06	0.014	0.011781	0.011419	1.83	-0.719	-0.596569	-0.613946
2.05	0.020	0.020658	0.020122	1.82	-1.470	-1.371522	-1.391980
2.04	0.035	0.035325	0.034566	1.81	-2.078	-2.010389	-2.031577
2.03	0.059	0.058867	0.057849	1.80	-2.491	-2.457481	-2.477546
2.02	0.095	0.095537	0.094261	1.79	-2.688	-2.686153	-2.704034
2.01	0.151	0.150896	0.149423	1.78	-2.689	-2.700982	-2.716562
2.00	0.233	0.231764	0.230360	1.77	-2.501	-2.534047	-2.547756
1.99	0.348	0.345853	0.344631	1.76	-2.201	-2.235744	-2.248227
1.98	0.504	0.500958	0.500499	1.75	-1.818	-1.863551	-1.875505
1.97	0.708	0.703536	0.704518	1.74	-1.433	-1.471657	-1.483390
1.96	0.963	0.956833	0.960018	1.73	-1.072	-1.103003	-1.114397
1.95	1.272	1.258309	1.264547	1.72	-0.766	-0.785315	-0.796074
1.94	1.635	1.597440	1.607336	1.71	-0.521	-0.531419	-0.541082
1.93	1.943	1.953361	1.967299	1.70	-0.335	-0.341828	-0.350018
1.92	2.292	2.294674	2.312366	1.69	-0.206	-0.208976	-0.215499
1.91	2.587	2.580447	2.600903	1.68	-0.121	-0.121373	-0.126257
1.90	2.763	2.764244	2.785738	1.67	-0.067	-0.066940	-0.070369
1.89	2.794	2.800467	2.820795	1.66	-0.035	-0.035034	-0.037293
1.88	2.639	2.652923	2.669530	1.65	-0.017	-0.017386	-0.018783
1.87	2.282	2.302987	2.313657	1.64	—	-0.008173	-0.008985

(DCP) values taken from Patil (1978).

Table 3b. SnO ($D^1\Pi$) Eigen function $v' = 1$

Inter-nuclear distance r	RKR (DCP)	MKN new approximation	MKN Langer (1949)	Inter-nuclear distance r	RKR (DCP)	MKN new approximation	MKN Langer (1949)
2.25	—	0.003310	0.001474	2.00	2.265	2.241482	2.263870
2.24	—	0.005467	0.002639	1.99	1.915	1.884761	1.892248
2.23	—	0.008886	0.004627	1.98	1.447	1.410453	1.401393
2.22	—	0.014210	0.007964	1.97	0.884	0.842359	0.818440
2.21	—	0.022353	0.013359	1.96	0.263	0.215507	0.181186
2.20	0.033	0.034573	0.021981	1.95	-0.377	-0.428473	-0.466148
2.19	0.048	0.052559	0.035389	1.94	-1.124	-1.040720	-1.077368
2.18	0.071	0.078509	0.055734	1.93	-1.646	-1.580842	-1.610311
2.17	0.106	0.115168	0.085836	1.92	-2.057	-2.011753	-2.031440
2.16	0.154	0.165864	0.129237	1.91	-2.337	-2.309145	-2.319466
2.15	0.220	0.234349	0.190156	1.90	-2.473	-2.462748	-2.467035
2.14	0.307	0.324744	0.273318	1.89	-2.471	-2.476906	-2.480397
2.13	0.420	0.441049	0.383588	1.88	-2.352	-2.368598	-2.377238
2.12	0.560	0.586738	0.525399	1.87	-2.147	-2.164373	-2.183214
2.11	0.733	0.763980	0.701922	1.86	-1.858	-1.895691	-1.927880
2.10	0.940	0.972902	0.914068	1.85	-1.591	-1.594486	-1.640731
2.09	1.173	1.210592	1.159374	1.84	-1.262	-1.289542	-1.347958
2.08	1.424	1.470280	1.430928	1.83	-0.986	-1.003467	-1.070284
2.07	1.689	1.740634	1.716631	1.82	-0.740	-0.751535	-0.821982
2.06	1.988	2.005721	1.998989	1.81	-0.535	-0.541754	-0.610968
2.05	2.228	2.245019	2.255231	1.80	-0.376	-0.375843	-0.439684
2.04	2.421	2.435019	2.459551	1.79	-0.252	-0.250834	-0.306438
2.03	2.549	2.550622	2.584657	1.78	-0.164	-0.160969	-0.206866
2.02	2.577	2.568337	2.605337	1.77	-0.103	-0.099271	-0.135272
2.01	2.487	2.469058	2.501947	1.76	-0.062	-0.058790	-0.085685

(DCP) values taken from Patil (1978)

Table 4. $D^1\Pi - X^1\Sigma$ system of SnO.

Band $v'-v''$	Franck-Condon Factors				r -Centroids in Å			
	RKR (DCP)	MKN Present work		Morse (DCP)	RKR (DCP)	MKN Present work		Morse (DCP)
		New approxi- mation	Langer (1949)			New approxi- mation	Langer (1949)	
0-0	0.125	0.129	0.136	0.131	1.889	1.889	1.888	1.888
0-1	0.275	0.274	0.275	0.271	1.909	1.923	1.923	1.922
0-2	0.275	0.280	0.284	0.275	1.957	1.956	1.956	1.956
0-3	0.187	0.178	0.191	0.185	1.989	1.989	1.989	1.988
0-4	0.087	0.084	0.095	0.089	2.022	2.028	2.022	2.014
0-5	0.029	0.034	0.035	0.031	2.059	2.054	2.056	2.040
1-0	0.246	0.248	0.267	0.256	1.865	1.864	1.926	1.864
1-1	0.158	0.139	0.139	0.158	1.902	1.898	1.901	1.903
1-3	0.099	0.091	0.090	0.093	1.966	1.965	1.925	2.014
1-4	0.202	0.206	0.201	0.193	1.992	1.994	1.997	1.996
1-5	0.172	0.171	0.188	0.156	2.031	2.032	2.029	2.038
1-6	0.090	0.100	0.111	0.092	2.067	2.061	2.060	2.069
2-0	0.254	0.249	0.273	0.259	1.843	1.841	1.839	1.839
2-2	0.128	0.123	0.121	0.124	1.908	1.908	1.908	1.914
2-3	0.094	0.093	0.100	0.093	1.942	1.941	1.942	1.964
2-5	0.082	0.079	0.078	0.084	2.010	2.007	2.010	1.997
2-6	0.174	0.166	0.183	0.181	2.041	2.042	2.044	2.016

(DCP) values taken from Patil (1978).

The eigenfunctions determined using the new approximation method and the method due to Langer were used to compute the r -centroids. Integrals were computed by numerical integration. These results have been recorded in table 4. Values obtained using the Morse-oscillator model and RKR procedure (Patil 1978) have been recorded for comparison.

6. Conclusions

The well-known Wentzel-Kramers-Brillouin (wKB) method can be employed along with realistic RKR potential for computing wavefunctions. These are considered as true wavefunctions. The FC factors and r -centroids evaluated with these wavefunctions are taken as standard results with which we could compare our results.

A critical examination of table 1 indicates that the MKN function is superior to the Morse function which predicts widely different turning points. This superiority is more clearly noticed for the $B^2\Sigma$ LaO. In the case of $D^2\Sigma$ AlO the agreement is far superior in the region $r > r_e$ to that in $r < r_e$, whereas in $B^2\Sigma$ LaO the agreement is equally good in both regions.

Tables 2a and 2b show that the MKN function predicts $U(r)$ values fairly well.

The percentage deviation of the factor $|U(\text{MKN}) - U(\text{obs})|$ throughout the range of r values varies from

0.08% to 0.57% in $X^1\Sigma$ SiO,

0.10% to 0.46% in $X^1\Sigma$ GeO,

0.23% to 1.95% in $X^1\Sigma$ SnO,

0.36% to 1.39% in $D^1 \Pi$ SnO

Tables 2a and 2b also reveal that the MKN oscillator model and the Hulbert-Hirschfelder model potential are almost equivalent; however one feels that for $X^1\Sigma$ and $D^1\Pi$ SnO the MKN potential is slightly better whereas the (H-H) potential is slightly superior in $X^1\Sigma$ electronic states of GeO and SiO. However the average performance of these two potentials is equally encouraging.

A critical survey of tables 3a and 3b shows that agreement between the new approximation method and Langer's method is extremely good. However on comparison with the RKR results, the new approximation method is slightly better.

The FC factors reveal that the result of the new approximation method applied to MKN model agree fairly well with the RKR values, and slightly superior to the Morse model results for a few transitions, and almost equivalent for other transitions. Results due to Langer's method are a little higher.

As expected, the agreement of r -centroids computed using the new method and Langer's method with RKR results is very good. Further work to explore the MKN function is in progress.

References

- Dunham J L 1932 *Phys. Rev.* **41** 713 and 721
 Herzberg G 1950 *Molecular spectra and molecular structure I* 2nd edn. (New York: van Nostrand).
 Hulbert and Hirschfelder 1941 *J. Chem. Phys.* **9** 61
 Langer R E 1949 *Phys. Rev.* **75** 1573
 Morse P M 1929 *Phys. Rev.* **34** 57
 Murthy N S and Murthy B N 1970 *J. Phys. B Atom. Molec. Phys.* **3L** 15
 Patil D C 1978 *Comparative study of transition probabilities of diatomic molecules* Ph. D. Thesis, Karnatak University, Dharwad
 Patil D C and Korwar V M 1978 *Acta Phys. Acad.* **44** 371
 Steele D, Lippincott E R and Vanderslice J T 1962 *Rev. Mod. Phys.* **34** 239
 Tawde N R and Tulasigeri V G 1972 *J. Phys. B Atom. Molec. Phys.* **B5** 1681
 Tietz T 1970 *Acta Phys. Acad.* **29** 391
 Varshni Y P 1957 *Rev. Mod. Phys.* **29** 664