

LETTERS TO THE EDITOR

CENTRIFUGAL DISTORTION CONSTANTS AND THERMODYNAMIC FUNCTIONS OF C_2H_4O , C_2D_4O AND C_2H_4S

The centrifugal distortion constants of ethylene oxide, ethylene oxide- d_4 and ethylene sulphide are evaluated for the first time using the relations given by Kivelson and Wilson¹ and Cyvin *et al.*² and presented in Table I. The centrifugal stretching coefficients D_j , D_K , D_{JK} , R_s , R_6 and δ_j which are the linear combinations of the 7 elements are also calculated and given in Table II.

TABLE I
Centrifugal Distortion constants in KHz

7 elements	C_2H_4O	C_2D_4O	C_2H_4S
τ_{xxxx}	— 62.9021	—46.8963	— 4.1657
τ_{yyyy}	— 12.0013	— 9.9166	— 1.4650
τ_{zzzz}	—153.9810	—59.3429	—187.9680
τ_{xyxy}	— 1.4276	— 5.0326	— 0.0860
τ_{yzyz}	— 9.7603	— 6.9583	— 2.6048
τ_{xxzz}	— 17655.8	— 1081.7	— 31.6780
τ_{xyyz}	— 13.0950	— 6.2150	— 1.8535
τ_{xxzz}	35.1688	16.6080	13.3144
τ_{xyyz}	— 0.0467	— 0.0900	— 0.0485
τ_{yyzz}	— 24.8098	—15.4949	— 2.9902
τ_{yyyz}	— 0.0243	— 0.0234	— 0.0408
τ_{zzyz}	0.0194	0.0226	— 0.3288
τ_{zzzz}	10.5110	1.3571	0.0092

TABLE II
Centrifugal stretching coefficients in KHz

Coefficient	C_2H_4O	C_2D_4O	C_2H_4S
D_j	8.0191	6.3437	0.6545
D_K	—8783.7	—522.87	33.0862
D_{JK}	8814.2	531.36	13.2513
R_s	—2200.4	—131.18	— 2.5307
R_6	—0.6719	—0.3789	— 0.0247
δ_j	3.1813	2.3112	0.1688

In general, the magnitudes of the centrifugal distortion constants appear to decrease as the molecular weight increases. Since all the molecules under study are asymmetric rotors, all the six centrifugal stretch-

ing coefficients exist. D_j is positive for all the molecules. This indicates that the centrifugal forces about any given axis will always tend to increase the moment of inertia about that axis which in turn decreases the effective rotational constant. It is observed that the centrifugal stretching coefficients are very sensitive to the mass of the molecules and that their magnitudes decrease rapidly as the mass of the molecules increases.

The values of the centrifugal distortion constants can be used for the microwave spectral analysis of these molecules. The experimental values of the centrifugal distortion constants are often used as additional information for accurate determination of the force field of a molecule. But, in the present case, such values are not available. However, since the force field used fairly reproduces the observed vibrational frequencies, the present values of the centrifugal distortion constants could be treated as sufficiently accurate.

The thermodynamic functions of the isotopic molecules, C_2H_4O and C_2D_4O are calculated after making corrections for anharmonicity and non-rigidity of the molecules. The thermodynamic functions of the other molecule, C_2H_4S are calculated assuming a rigid rotor harmonic oscillator approximation. The values of these functions are given in Tables III, IV and V respectively.

TABLE III
Thermodynamic functions of C_2H_4O in cal. deg⁻¹ mole⁻¹

Temperature ° K	Heat content	Free energy	Entropy	Heat capacity
100	7.96	41.04	48.99	7.95
200	8.09	46.57	54.66	8.83
273.2	8.53	49.15	57.68	10.82
298.15	8.74	49.90	58.64	11.61
300	8.77	49.96	58.73	11.70
400	9.96	52.64	62.59	15.23
500	11.33	55.00	66.33	18.37
600	12.73	57.19	69.92	20.94
700	14.04	59.31	73.35	23.09
800	15.28	61.19	76.47	24.86
900	16.45	63.07	79.52	26.39
1000	17.52	64.87	82.39	27.70

TABLE IV

Thermodynamic functions of C_2D_4O in cal. deg⁻¹ mole⁻¹

Temperature °K	Heat content	Free energy	Entropy	Heat capacity
100	7.96	41.93	49.88	8.01
200	8.43	47.53	55.72	9.53
273.2	9.18	50.43	59.41	12.90
298.15	9.52	50.90	60.42	13.94
300	9.57	51.20	60.65	14.04
400	11.20	54.31	65.50	18.04
500	12.90	56.75	69.65	21.30
600	14.51	59.24	73.75	23.94
700	16.03	61.60	77.64	26.59
800	17.40	63.84	81.24	27.84
900	18.65	65.96	84.61	29.28
1000	19.77	67.53	87.29	30.44

TABLE V

Thermodynamic functions of C_2H_4S in cal. deg⁻¹ mole⁻¹

Temperature °K	Heat content	Free energy	Entropy	Heat capacity
100	7.95	43.78	51.73	7.99
200	8.29	49.35	57.64	9.73
273.2	9.00	52.03	61.03	12.30
298.15	9.28	52.54	61.92	13.22
300	9.34	52.89	62.23	13.32
400	10.80	55.77	66.57	16.95
500	12.35	58.35	70.69	19.93
600	13.80	60.73	74.53	22.26
700	15.16	62.96	78.13	24.19
800	16.39	65.07	81.46	25.77
900	17.51	67.06	84.57	27.15
1000	18.52	68.93	87.45	28.31

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ON THE D ¹Π - X ¹Σ TRANSITION OF SnO

Introduction

WHILE working on D ¹Π - X ¹Σ transition of SnO, it was noticed by us that some of the results of Dube and Rai¹, who have worked on this transition recently, were erroneous. The corrected results with R. K. R. potentials have been reported in a detailed paper to be published elsewhere. The present work is just a follow up of the same work using another approximate method.

Recently Herman *et al.*² have proposed a new method of calculating vibrational wave functions for diatomic molecules. We have employed this method to evaluate wave functions for some vibrational states involved in the D ¹Π - X ¹Σ transition of SnO. Franck-Condon factors (FCFs) have then been computed and their results compared with our corresponding RKR results reported elsewhere.

Method of Herman *et al.*²

By an iteration process Herman *et al.*² solve the Schrödinger equation

$$\frac{d^2\psi_v}{dx^2} + \{[E - V(x)]/B_e\} \psi_v(x) = 0 \quad (1)$$

Here

$$x = \frac{r - r_e}{r_e};$$

r = internuclear separation,

r_e = equilibrium internuclear separation,

B_e = equilibrium rotational constant,

E = vibrational eigen energy.

Equation (1) is solved by making the following transformations :

$$\psi_0(x) = \exp - \frac{1}{2} \left\{ \int_0^x y(x') dx' \right\} \quad (2)$$

is the unnormalized wave function of the ground state $v = 0$

$$\psi_v(x) = g_v(x) \psi_0(x). \quad (3)$$

The functions $y(x)$ and $g_v(x)$ themselves, in turn, satisfy the equations:

$$y^2(x) - \left[\frac{2dy(x)}{dx} \right] - \frac{4}{B_e} [V(x) - E_v] = 0 \quad (4)$$

and

$$\frac{d^2g_v}{dx^2} - y(x) \frac{dg_v(x)}{dx} + \frac{E_v - E_0}{B_e} g_v(x) = 0. \quad (5)$$

Power-series solutions to equations (4) and (5) have been found by Herman *et al.*; these have been tabulated by Herman *et al.*².

TABLE I
 $D^1\Pi - X^1\Sigma$ transition of $\tilde{S}nO$ using Iteration method

Band	Franck-Condon factors			r-centroids		
	RKR potentials	Rydberg potential	Varshni's potential	RKR potentials	Rydberg potential	Varshni's potential
0,0	0.1255	0.1328	0.1346	1.8891	1.8876	1.8862
0,1	0.2748	0.2680	0.2577	1.9093	1.9221	1.9193
0,2	0.2754	0.2726	0.2623	1.9579	1.9553	1.9963
0,3	0.1872	0.1826	0.1739	1.9888	1.9876	1.9871
0,4	0.0871	0.0863	0.0942	2.0222	2.0215	1.9473
0,5	0.0292	0.0221	0.0379	2.0592	2.0807	2.0458
1,0	0.2459	0.2602	0.2765	1.8648	1.8633	1.8614
1,1	0.1580	0.1516	0.1340	1.9020	1.8623	1.9006
1,3	0.0992	0.0868	0.0657	1.9664	1.9642	1.9591
1,4	0.2016	0.1866	0.1600	1.9919	1.9945	2.0987
1,5	0.1723	0.1804	0.1626	2.0314	2.0207	2.0182
2,0	0.2537	0.2625	0.2766	1.8427	1.8384	1.8352
2,2	0.1281	0.1230	0.1233	1.9075	1.9078	1.9062
2,3	0.0939	0.0944	0.0898	1.9419	1.9358	1.9572
2,5	0.0821	0.0650	0.0469	2.0103	2.0010	1.9929

Results and Discussion

In the present work we have employed two potentials defined by the following relations:

$$V(r) = -D [1 + a(r - r_e)] e^{a(r - r_e)} \quad (6)$$

(Rydberg potential)

$$V(r) = D [1 - e^{-b(r^2 - r_e^2)}]^2 \quad (7)$$

(Varshni's potential)³

Vibrational wave functions have been computed for the following vibrational states:

$$D^1\Pi \text{ state; } v = 0 \ 1 \ 2$$

$$X^1\Sigma \text{ state; } v = 0 \ 1 \ 2 \ 3 \ 4 \ 5$$

Using these wave functions FCFs have been determined. These are tabulated in Table I. In the same table are listed our RKR results for comparison.

Electron transition moment variation and the effective vibrational temperature on RKR potentials have been evaluated and reported by us earlier. We give here these results for comparison with the ones determined by Rydberg potential using the iteration method proposed by Herman *et al.*²

$$R_e(r) = \text{constant } X [1 - 1.022r + 0.261r^2]$$

with RKR potentials

and

$$T = 1919^\circ \text{ k}$$

$$R_e(r) = \text{constant } X [1 - 1.034r + 0.266r^2]$$

with Rydberg potential

and

$$T = 1740^\circ \text{ k.}$$

Taking RKR FCFs as standard results, if one compares the other two sets of results it is clear that Rydberg potential has yielded better FCFs than the other potential proposed by Varshni³. It is, therefore, only the Rydberg FCFs that have been employed to obtain $R_e(r)$ variation for comparison with the corresponding RKR result. It is also seen that the two expressions for $R_e(r)$, the one on RKR FCFs and the other on Rydberg FCFs compare favourably with each other. Thus we have found in the present work that Rydberg potential is almost as good as RKR potentials at least at low vibrational quantum numbers.

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