Molecular Constants of Some Alkali Metal Halide Dimers by Kinetic Constants Method

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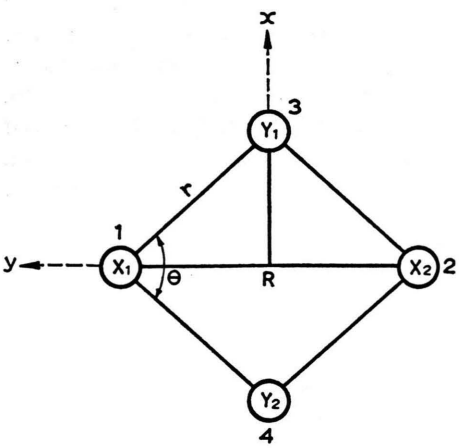
Z. Naturforsch. **36a**, 975–979 (1981); received June 24, 1981

The kinetic constants method is employed to obtain a fresh set of potential constants in the case of nine X_2Y_2 type (D_{2h} symmetry) alkali metal halide dimers. The mean amplitudes of vibration, Coriolis coupling constants, Centrifugal distortion constants and thermodynamic functions are evaluated with the presently obtained potential constants. The results are briefly discussed.

Introduction

In recent years, the kinetic constants method based on Wilson's group theoretical approach [1] has been found to be a very useful tool in the evaluation of potential constants. The present paper is a continuation of our studies [2–7] on different molecular systems by the kinetic constants method. A normal coordinate analysis of Li_2F_2 was carried out by Snelson et al. [8], and computations of mean amplitudes of vibration of these dimers were carried out by Cyvin and Cyvin [9].



GEOMETRY OF X_2Y_2 (D_{2h}) TYPE MOLECULES

Figure 1

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The molecules under study have a planar, rhombic D_{2h} structure. The six vibrational modes are classified as

$$\Gamma_{vib} = 2A_g + B_{1g} + B_{1u} + B_{2u} + B_{3u}.$$

The gerade modes are Raman active and the ungerade modes infrared active. The frequencies, which are theoretical values based on model computations, and the molecular parameters employed are taken from Trugmon and Gordon [10]. The symmetry coordinates are taken from Lesiecki and Nibbler [11]. Figure 1 gives the geometrical parameters of the X_2Y_2 systems.

Evaluation of Kinetic and Potential Constants

The elements of the kinetic energy matrix are used to arrive at the kinetic constants [12].

Thirugnanasambandam and Srinivasan [13] proposed to utilise K_{ij}'s as additional constraints, due to marked similarities in K_{ij} and F_{ij} for the 2×2 species. The secular equation is solved using the above constraint. For other single species the force constants are obtained using the relation $F_{ii} = \lambda_i K_{ii}$.

Mean Amplitudes of Vibration

Mean amplitudes of vibrations are calculated using Cyvin's relation [14] $\sum = L \Delta L'$, where L's are characteristic vectors, L''s their transpose and Δ a diagonal matrix. The Δ elements are given by $\Delta_i = (h/8\pi^2\nu_i) \coth (h\nu_i/2kT)$.

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Coriolis Coupling Constants

The Coriolis matrix elements C_{ij}^{α} ($\alpha = x, y, z$) are obtained by using the vector method of Meal and Polo [15]; they are

$$C_{1,3}^{z} = \sin\theta\,(\mu_x + \mu_y),$$
$$C_{2,3}^{z} = 2\sin(\theta/2)\,\mu_x,$$
$$C_{5,6}^{z} = \sin\theta\,(\mu_x + \mu_y),$$
$$C_{4,6}^{y} = \sin(\theta/2)\,(\mu_x + \mu_y),$$
$$C_{4,5}^{x} = -\cos(\theta/2)\,(\mu_x + \mu_y).$$

The active couplings are $A_g \times B_{1g}$ pertaining to the first two elements and $B_{2u} \times B_{3u}$ pertaining to the remaining elements. The Coriolis coupling coefficient matrix ζ^{α} is related to C^{α} by

$$\zeta^{\alpha} = L^{-1} C^{\alpha} (L')^{-1}.$$

Centrifugal Distortion Constants

Cyvin et al. [16] reformulated the theory of centrifugal distortion by introducing certain new elements $T_{\alpha\beta,S}$ instead of the partial derivative inertia tensor components $J_{\alpha\beta,S}$ of Kivelson and Wilson [17, 18]. The quantities $t_{\alpha\beta\gamma\delta}$ are determined by making use of Cyvin's relation, and hence τ values are evaluated. The centrifugal stretching coefficients D_J, D_K, D_{JK}, R_5 R_6, and δ_J are linear combinations of τ elements. These coefficients are evaluated by using the relations given by Kivelson and Wilson.

Thermodynamic Functions

The thermodynamic functions are evaluated for temperatures ranging from 100 K to 1000 K, assuming the rigid rotor, harmonic oscillator model [19].

Results and Discussion

The evaluated potential constants are presented in Table 1, along with the values obtained by Kumar et al. [20] for comparison. The variation in the f_r values is as expected, except in the case of Rb_2F_2. The variation is in accordance with the observations made by Kumar et al. [20]. From Table 1 it can also be noted that the stretching force constant decreases as the mass of the Y atom increases. This is in accordance with the decrease in electronegativity and increase in atomic radius from F to Br.

The calculated mean amplitudes of vibration are given in Table 2 for 0, 298.15 and 500 K. The values obtained by Kumar et al. [20] and Cyvin and Cyvin [9] are included for comparison. The mean amplitudes of non bonded atom pairs are in general greater than those for bonded atom pairs. However in case of Li_2F_2, Li_2Cl_2 and Li_2Br_2 it is observed that $U_{Y\ldots Y} < U_{X-Y}$, which is a low temperature anomaly as pointed out by Cyvin and Cyvin [9]. A similar low temperature anomaly is also observed presently in the case of Rb_2F_2 ($U_{X\ldots X} < U_{X-Y}$). Experimental mean amplitudes of vibration for

Table 1. Force constants (m dyn/Å).

Molecule	f_r	f_{rr}	f'_{rr}	f''_{rr}	f_R	$-f_{rR}$	f_{op}
Li_2F_2	1.508 (1.367)	0.541 (0.461)	0.509 (0.297)	0.328 (0.177)	1.221 (1.319)	0.630 (0.526)	0.777 (0.776)
Li_2Cl_2	0.753 (0.667)	0.305 (0.235)	0.297 (0.194)	0.213 (0.126)	0.551 (0.595)	0.328 (0.272)	0.350 (0.349)
Li_2Br_2	0.681	0.284	0.279	0.213	0.435	0.286	0.275
Na_2F_2	0.890 (0.869)	0.147 (0.138)	0.142 (0.110)	0.048 (0.027)	0.616 (0.621)	0.195 (0.165)	0.389 (0.388)
Na_2Cl_2	0.507 (0.484)	0.104 (0.080)	0.104 (0.081)	0.053 (0.030)	0.334 (0.342)	0.143 (0.120)	0.203 (0.202)
K_2F_2	0.719 (0.713)	0.083 (0.078)	0.082 (0.078)	0.017 (0.012)	0.401 (0.401)	0.093 (0.082)	0.260 (0.258)
K_2Cl_2	0.495 (0.486)	0.060 (0.047)	0.060 (0.057)	0.021 (0.012)	0.250 (0.251)	0.085 (0.073)	0.159 (0.158)
Rb_2F_2	0.753 (0.751)	0.068 (0.062)	0.067 (0.071)	0.013 (0.012)	0.328 (0.327)	0.042 (0.040)	0.210 (0.210)
Rb_2Cl_2	0.373 (0.371)	0.041 (0.034)	0.041 (0.044)	0.009 (0.007)	0.197 (0.197)	0.041 (0.037)	0.133 (0.132)

Values in paranthesis are from [20].

Table 2. Mean amplitudes of vibration (Å).

Molecule	U_{X-Y}			$U_{X\ldots X}$			$U_{Y\ldots Y}$		
	0 K	298.15 K	500 K	0 K	298.15 K	500 K	0 K	298.15 K	500 K
Li_2F_2	0.073	0.078	0.088	0.091	0.098	0.112	0.061	0.068	0.080
	—	(0.079)	(0.089)	—	(0.084)	(0.093)	—	—	—
	0.078 *	0.085 *	0.098 *	0.094 *	0.101 *	0.116 *	0.072 *	0.087 *	0.106 *
	—	0.070 **	—	—	—	—	—	—	—
Li_2Cl_2	0.086	0.101	0.121	0.111	0.136	0.165	0.063	0.089	0.111
	—	(0.101)	(0.128)	—	(0.124)	(0.132)	—	—	—
Li_2Br_2	0.087	0.111	0.128	0.116	0.152	0.187	0.054	0.097	0.124
Na_2F_2	0.067	0.080	0.096	0.073	0.098	0.121	0.077	0.102	0.126
	—	(0.080)	(0.096)	—	(0.093)	(0.116)	—	—	—
	0.070 *	0.087 *	0.107 *	0.071 *	0.092 *	0.113 *	0.075 *	0.093 *	0.115 *
Na_2Cl_2	0.072	0.102	0.128	0.088	0.139	0.176	0.075	0.125	0.159
	—	(0.102)	(0.128)	—	(0.130)	(0.164)	—	—	—
K_2F_2	0.066	0.084	0.103	0.068	0.110	0.132	0.086	0.127	0.160
	—	(0.084)	(0.103)	—	(0.108)	(0.138)	—	—	—
K_2Cl_2	0.066	0.098	0.124	0.078	0.144	0.185	0.081	0.150	0.190
	—	(0.099)	(0.124)	—	(0.140)	(0.179)	—	—	—
Rb_2F_2	0.062	0.080	0.099	0.058	0.115	0.148	0.089	0.143	0.181
	—	(0.080)	(0.099)	—	(0.114)	(0.147)	—	—	—
Rb_2Cl_2	0.066	0.110	0.140	0.067	0.151	0.195	0.088	0.178	0.229
	—	(0.110)	(0.140)	—	(0.150)	(0.193)	—	—	—

Values in Paranthesis are from [20]. * Values from [9]. ** Assumed value in [21] and [22].

Li_2F_2 from modern structural studies have been reported by Solomonik et al. [23] at 1360 ± 50 °K. Table 3 gives the presently evaluated mean amplitudes for Li_2F_2 at 1360 °K along with these experimentally observed values.

The mean amplitudes of vibration increase with increase in temperature. They will be useful in the electron diffraction study of these molecules.

The evaluated Coriolis coupling constants are given in Table 4. It is observed from the table that the square sum rules

$$(\zeta^z_{1,3})^2 + (\zeta^z_{2,3})^2 = 1$$

and also

$$(\zeta^z_{5,6})^2 = (\zeta^x_{4,5})^2 = (\zeta^y_{4,6})^2 = 1$$

Table 3. Mean amplitudes of vibration for Li_2 F_2 at 1360 K (Å).

U_{X-Y}	$U_{X\ldots X}$	$U_{Y\ldots Y}$	Ref.
0.1322	0.1698	0.1238	P.W.
$0.112 \begin{smallmatrix} +0.011 * \\ -0.022 \end{smallmatrix}$	—	$0.236 \begin{smallmatrix} +0.018 * \\ -0.033 \end{smallmatrix}$	23

P.W.: Present work. *: Experimental values from Ref. (23).

Table 4. Coriolis coupling constants.

Molecule	$A_g \times B_{1g}$		$B_{2u} \times B_{3u}$
	$\zeta^z_{1,3}$	$\zeta^z_{2,3}$	$\zeta^z_{5,6} = \zeta^y_{4,6} = -\zeta^x_{4,5}$
Li_2F_2	0.464	0.887	1.000
Li_2Cl_2	0.672	0.740	1.000
Li_2Br_2	0.840	0.543	1.000
Na_2F_2	− 0.095	0.996	1.000
Na_2Cl_2	0.213	0.977	1.000
K_2F_2	− 0.346	0.938	1.000
K_2Cl_2	− 0.049	0.999	1.000
Rb_2F_2	− 0.636	0.771	1.000
Rb_2Cl_2	− 0.414	0.911	1.000

Table 5. Centrifugal distortion coefficients (kHz).

Molecule	D_J	D_K	$-D_{JK}$	R_5	R_6	δ_J
Li_2F_2	1.055	44.447	4.547	0.803	0.038	0.324
Li_2Cl_2	0.216	24.696	2.149	0.189	0.004	0.047
Li_2Br_2	0.046	20.594	1.141	0.041	0.000	0.005
Na_2F_2	0.671	3.293	1.835	0.392	0.072	0.353
Na_2Cl_2	0.154	1.319	0.525	0.111	0.013	0.074
K_2F_2	0.165	2.418	0.757	0.132	0.011	0.072
K_2Cl_2	0.097	0.518	0.307	0.066	0.012	0.053
Rb_2F_2	0.033	1.947	0.350	0.031	0.001	0.009
Rb_2Cl_2	0.020	0.423	0.112	0.017	0.001	0.008

Table 6. Thermodynamic functions (Cal K^{-1} mol^{-1}).

Molecule	Thermo-dynamic function	100 K	298.15 K	400 K	600 K	800 K	1000 K
Li_2F_2	C_P	8.53	14.89	16.61	18.25	18.92	19.25
	F	43.17	52.93	56.20	61.43	65.59	69.26
	H	8.05	10.57	11.88	13.79	15.01	15.84
	S	51.22	63.50	68.08	75.23	80.60	85.10
Li_2Cl_2	C_P	10.70	17.44	18.41	19.19	19.48	19.62
	F	47.27	58.72	62.64	68.74	73.43	77.14
	H	8.67	12.81	14.11	15.71	16.63	17.21
	S	55.93	71.52	76.75	84.45	90.07	94.34
Li_2Br_2	C_P	11.83	17.94	18.64	19.29	19.54	19.65
	F	51.60	63.87	68.01	74.36	79.07	83.01
	H	9.24	13.56	14.78	16.23	17.02	17.55
	S	60.84	77.43	82.79	90.60	96.09	100.56
Na_2F_2	C_P	11.19	17.78	18.64	19.29	19.54	19.65
	F	47.51	59.31	63.39	69.56	74.32	78.06
	H	8.86	13.20	14.49	16.00	16.86	17.40
	S	56.37	72.51	77.88	85.55	91.17	95.46
Na_2Cl_2	C_P	14.40	18.96	19.35	19.63	19.74	19.78
	F	51.37	65.34	69.91	76.70	81.84	85.81
	H	10.37	15.15	16.17	17.29	17.90	18.25
	S	61.74	80.49	86.08	93.99	99.74	104.07
K_2F_2	C_P	12.78	18.44	19.04	19.48	19.65	19.72
	F	50.41	63.35	67.69	74.13	79.19	90.95
	H	9.62	14.23	15.38	16.67	17.43	17.85
	S	60.03	77.58	83.07	90.80	96.61	100.86
K_2Cl_2	C_P	15.36	19.17	19.47	19.69	19.77	19.80
	F	53.88	68.58	73.35	80.30	85.48	89.16
	H	11.09	15.71	16.63	17.62	18.15	18.45
	S	64.98	84.29	89.97	97.92	103.63	107.61
Rb_2F_2	C_P	13.54	18.63	19.16	19.53	19.68	19.75
	F	54.37	67.88	72.36	78.96	84.00	88.08
	H	10.20	14.69	15.77	16.95	17.63	18.07
	S	64.57	82.57	88.13	95.91	101.63	106.15
Rb_2Cl_2	C_P	16.89	19.46	19.63	19.77	19.81	19.83
	F	57.98	73.93	78.85	86.30	90.92	94.28
	H	12.35	16.60	17.33	18.15	18.51	18.72
	S	70.33	90.53	96.18	104.45	109.44	113.01

C_P = Heat Capacity; F = Free Energy; H = Heat content; S = Entropy.

are satisfied for all the dimers. These constants are useful in the interpretation of vibration-rotation interaction studies of these dimers.

Table 5 gives centrifugal distortion coefficients obtained presently. The distortion coefficients, in general, decrease with increase in the mass of the system and are very sensitive to the mass. The sum rules given by Kivelson and Wilson [17] in case of "t" elements are found to be satisfied.

The evaluated thermodynamic functions of these dimers are given in Table 6. The thermodynamic functions increase with increase in temperature.

Acknowledgement

The authors wish to thank Prof. D. K. P. Varadarajan, Principal and the Management of PSG College of Arts and Science (Autonomous) Coimbatore, for their constant encouragement. The authors take this opportunity to thank the learned referee for his valuable suggestions and comments.

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