

True potential energy curves, r -centroids and Franck-Condon factors of a few transition metal diatomic molecules

M V RAMANAIAH and S V J LAKSHMAN

Department of Physics, Sri Venkateswara University, Tirupati 517 502, India

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Abstract. The true potential energy curves for some electronic states of CuF, CuO, CuSe and CuTe molecules have been constructed by the method of Lakshman and Rao (RKR method as modified by Lakshman and Rao). The ground-state dissociation energies evaluated by the method of curve fitting using the H-H function agree well with the values reported earlier. The r -centroids and Franck-Condon factors for various band systems of the above diatomic molecules have been computed.

Keywords. Potential energy curves; dissociation energy; r -centroids; Franck-Condon factors; transition metals; diatomic molecules.

1. Introduction

Diatomic molecules containing at least one transition metal atom are of interest because they represent the simplest systems in which to study the effects of d electrons on bonding (Cheetham and Barrow 1967).

Woods (1943) observed three band systems designated as $A^1\Pi - X^1\Sigma$, $B^1\Sigma - X^1\Sigma$ and $C^1\Pi - X^1\Sigma$ lying at $\lambda\lambda 5700 \text{ \AA}$, $\lambda 5060 \text{ \AA}$ and $\lambda 4920 \text{ \AA}$, for the CuF molecule while studying the emission spectrum of HF. He has rotationally analysed the systems and found that all the three systems have the same lower state.

The various band systems of the CuO molecule have been studied by Lagerqvist and Uhler (1967), Antic-Jovanovic *et al* (1968), Antic-Jovanovic and Pesic (1973), Appelblad and Lagerqvist (1973a, 1973b and 1974), Thompson *et al* (1973) and Lefebvre *et al* (1976).

A number of bands of $^{63}\text{Cu}^{80}\text{Se}$ in the region $\lambda\lambda 6670-5335 \text{ \AA}$ were observed in the spectrum of mixed vapours of selenium and copper and were classified into two systems *viz* $A-X$ and $B-X$ by Joshi (1962). Later Lefebvre and Bocquet (1976) performed the vibrational and rotational analyses of the visible band system of this molecule.

Emission spectrum of the CuTe molecule was observed in the region $\lambda\lambda 6945-6110 \text{ \AA}$ by Maheswari and Sharma (1963). The vibrational and rotational analyses have been performed by Lefebvre and Bocquet (1975).

The vibrational and rotational constants required for the present work are shown in table 1.

Since only B_0 values are available for $A^1\Pi$ of CuF, and $A^2\Sigma^+$ and $X^2\Pi_i$ of CuSe molecules, the values of B_e , α_e and r_e for these electronic states were calculated using Pekeris relation (Lakshman and Venkataramanaiah 1980).

Table 1. Molecular constants of CuF, CuO, CuSe and CuTe

Molecule and State	T_e cm^{-1}	ω_e cm^{-1}	$\omega_e X_e$ cm^{-1}	B_e cm^{-1}	α_e cm^{-1}	r_e (Å)	References
<u>CuF</u>							
$X^1\Sigma^+$	0	622.65	3.95	0.37940	0.00323	1.7449	Huber and Herzberg (1979)
$A^1\Pi$	17543.40	649.20	4.00	0.36750* (0.36890)	(0.00288) 0.00320	1.7730* (1.7695) 1.7630	
$B^1\Sigma^+$	19717.50	657.00	3.92	0.37160			
<u>CuO</u>							
$X_1^2\Pi_{3/2}$	0	640.17	4.43	0.44454	0.00456	1.7244	Lefebvre <i>et al</i> (1976)
$X_2^2\Pi_{1/2}$	279.02	636.18	4.36	0.44415	0.00449	1.7251	
$E^2\Delta_{5/2}$	21058.00	733.00	5.50	0.44450	0.00360	1.7244	Huber and Herzberg (1979)
<u>CuSe</u>							
$X^2\Pi_i$	0	302.37	0.99	0.10774* (0.10797)	(0.00047)	2.1081* (2.1059) 2.1699	Lefebvre and Bocquet (1976)
$A^2\Sigma^+$	17960.40	253.00	2.74	0.10169			
<u>CuTe</u>							
X	0	252.67	0.701	0.07025	0.00028	2.3490	Lefebvre and Bocquet (1975)
A	15991.92	200.58	2.009		0.00052	2.4310	

* Values of B_0 and r_0 . Calculated values of B_e and r_e using the method described in the text are shown in the paranthesis.

2. True potential energy curves

The present paper deals with the construction of potential energy curves for $X^1\Sigma^+$, $A^1\Pi$ and $B^1\Sigma^+$ states of the CuF molecule, $X^2\Pi_{3/2}$ and $E^2\Delta_{5/2}$ states of CuO, $X^2\Pi_i$ and $A^2\Sigma^+$ states of CuSe and X and A states of the CuTe molecule. The RKR method as modified by Lakshman and Rao (1971) has been used to construct potential energy curves.

3. Dissociation energy

The ground state dissociation energies of the CuF, CuO, CuSe and CuTe molecules have been evaluated by the curve fitting method. The potential energy curves for different molecular electronic states can be calculated theoretically by using the Hulburt-Hirschfelder (1941) function. This five-parameter function gives the best average results and in general gives the best fit of the potential. The turning points obtained in the present work were used in the above expression and the values of potential energy for different vibrational levels were calculated using different values of D_e . That value of D_e which gave the value close to the experimental value of U was chosen as the dissociation energy of the molecule. The values thus obtained for CuF, CuO, CuSe and CuTe are 35650 cm^{-1} (4.42 eV), 23000 cm^{-1} (2.8 eV), 20500 cm^{-1} (2.54 eV) and 18000 cm^{-1} (2.11 eV) respectively and are in good agreement with the values of 4.42, 2.79, 2.55 and 2.35 eV reported in Huber and Herzberg (1979).

4. r -centroids

The quadratic equation method of Nicholls and Jarman (1956) has been used to evaluate the r -centroids for all the systems for which the potential energy curves have been constructed. The present paper deals with the evaluation of the r -centroids of the A - X and B - X systems of CuF, A - X systems of CuSe and CuTe. The r -centroids and Franck-Condon factors of the above two systems are presented in tables 2, 4 and 5.

5. Franck-Condon factors

Franck-Condon factors have been evaluated by the method of Fraser and Jarman (1953) and are presented in tables 2 to 5. From the data on F-C factors, it can be concluded that

(i) In the case of A - X and B - X band systems of CuF and B - X system of CuO, it is not likely that the bands 4, 0 and beyond in the v' ($v'' = 0$) progression and 0, 3 and beyond in the v'' ($v' = 0$) progression be observed since the corresponding values of the Franck-Condon factors are either zero or too small.

(ii) Bands like 3, 2; 4, 1 and 5, 1 of the A - X system of CuSe which are not so far observed might be observed under improved experimental techniques.

(iii) It might be possible to observe bands like 3, 0; 4, 1; etc in the A - X system of CuTe in addition to a few more beyond 4, 0 in the v' progression with improved experimental work.

Table 2. r -centroids and Franck-Condon factors of the CuF Molecule

v' \ v''	0	1	2	3	4	5
<i>A¹Π-X¹Σ⁺ system</i>						
0 (a)	1.7550					
(b)	0.9213	0.0785	0.0001			
(c)	5694.3					
1 (a)	1.660	1.749				
(b)	0.0688	0.7822	0.1485	0.0003	0.0002	
(c)		5685.7				
2 (a)	1.601	1.656	1.743			
(b)	0.0085	0.1133	0.6664	0.2109	0.0004	0.0004
(c)			5677.2			
3 (a)	1.559	1.600	1.654	1.738		
(b)	0.0011	0.0213	0.1394	0.5701	0.2666	0.0006
(c)				5668.2		
4 (a)	1.526	1.559	1.599	1.652	1.732	
(b)	0.0002	0.0038	0.0355	0.1521	0.4900	0.3163
(c)					5660.4	
5 (a)	1.498	1.526	1.559	1.598	1.650	1.727
(b)		0.0007	0.0078	0.0492	0.1551	0.4236
(c)						5652.2
<i>B¹Σ⁺-X¹Σ⁺ system</i>						
0 (a)	1.749					
(b)	0.9555	0.0443	0.0001			
(c)	5061.2					
1 (a)	1.642	1.740				
(b)	0.0393	0.8753	0.0848	0.0004	0.0001	
(c)	4901.4	5052.3				
2 (a)	1.581	1.637	1.731			
(b)	0.0046	0.0664	0.8061	0.1217	0.0010	0.0002
(c)		4895.2	5043.5			
3 (a)	1.539	1.580	1.634	1.723		
(b)	0.0005	0.0118	0.0839	0.7465	0.1550	0.0016
(c)			4888.5	5034.8		
4 (a)	1.506	1.538	1.578	1.631	1.715	
(b)	0.0001	0.0018	0.0203	0.0938	0.6952	0.1850
(c)				4882.0	5026.2	
5 (a)	1.478	1.505	1.537	1.577	1.628	1.707
(b)		0.0003	0.0038	0.0292	0.0980	0.6513
(c)						

(a) r -centroid; (b) Franck-Condon factor; (c) Wavelength in Å

Table 3. Frank-Condon factors of the E-X system of CuO

v' \ v''	0	1	2	3	4	5
0	0.9977	0.0001	0.0021	0.0001	0.0000	0.0000
1	0.0001	0.9924	0.0012	0.0058	0.0005	0.0000
2	0.0022	0.0010	0.9808	0.0041	0.0105	0.0015
3	0.0001	0.0063	0.0031	0.9619	0.0099	0.0154
4	0.0000	0.0002	0.0123	0.0070	0.9347	0.0197
5	0.0000	0.0001	0.0003	0.0203	0.0129	0.8987

Table 4. r -centroids and F-C factors of the $A^2\Sigma^+ - X^2\Pi$, system of CuSe

v' \ v''		0	1	2	3	4	5
0	(a)	2.1386	2.2019	2.2651			
	(b)	0.6028	0.3108	0.0746	0.0108	0.0010	0.0001
	(c)	5574.1	5668.8	5766.3			
1	(a)	2.0849	2.1491	2.2176	2.2753	2.1334	
	(b)	0.2960	0.1423	0.3568	0.1642	0.0359	0.0047
	(c)	5498.0		5685.2	5782.7	5882.9	
2	(a)	2.0293	2.0965	2.1595	2.2213	2.2835	2.3473
	(b)	0.0816	0.3167	0.0050	0.2765	0.2330	0.0734
	(c)	5425.9	5515.6		5702.8	5800.5	5900.3
3	(a)	1.9679	2.0424	2.1079	2.1700	2.2311	2.2928
	(b)	0.0167	0.1653	0.2220	0.0227	0.1619	0.2645
	(c)		5444.6				5819.0
4	(a)	1.8871	1.9841	2.0553			
	(b)	0.0028	0.0508	0.2115	0.1104	0.0845	0.0661
	(c)		5376.7	5464.6			
5	(a)		1.9130	1.9925			
	(b)	0.0004	0.0116	0.0939	0.2108	0.0317	0.1399
	(c)			5398.0			

(a) r -centroid; (b) Franck-Condon factor; (c) Wavelength in Å**Table 5.** r -centroids and F-C factors of the $A-X$ system of CuTe

v' \ v''		0	1	2	3	4	5
0	(a)	2.3918	2.4393	2.4868	2.5348		2.6341
	(b)	0.3798	0.3762	0.1781	0.0530	0.0110	0.0017
	(c)	6263.5	6364.0	6466.9	6571.9		
1	(a)	2.3542	2.4022	2.4495	2.4968	2.5447	2.5936
	(b)	0.3520	0.0002	0.2058	0.2601	0.1325	0.0399
	(c)	6187.2	6285.2	6387.6	6487.9	6592.7	6701.0
2	(a)	2.3166	2.3655	2.4130		2.5073	
	(b)	0.1779	0.1685	0.0890	0.0388	0.2195	0.1955
	(c)	6113.0	6208.7	6307.0		6508.6	6613.7
3	(a)		2.3290			2.5183	
	(b)	0.0650	0.2261	0.0206	0.1603	0.0019	0.1220
	(c)		6134.4	6230.0	6330.2	6335.0	6640.0
4	(a)			2.3418			
	(b)	0.0192	0.1411	0.1546	0.0085	0.1308	0.0493
	(c)			6155.6			
5	(a)						
	(b)	0.0048	0.0603	0.1739	0.0580	0.0640	0.0582
	(c)						

(a) r -centroid; (b) Franck-Condon factor; (c) Wavelength in Å

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References

- Antic Jovanovic A, Pesic D S and Gaydon A G 1968 *Proc. Phys. Soc.* **A307** 399
Antic Jovanovic A and Pesic D S 1973 *J. Phys.* **B6** 2473
Appelblad O and Lagerqvist A 1973a *J. Mol. Spectrosc.* **48** 607
Appelblad O and Lagerqvist A 1973b *Can J. Phys.* **53** 2221
Appelblad O and Lagerqvist A 1974 *Phys. Scr.* **10** 307
Cheetham C J and Barrow R F 1967 *Advances in high temperature chemistry* (ed.) Eyring (New York, London: Academic Press) Vol. 1, p. 7
Fraser P A and Jarman W R 1953 *Proc. Phys. Soc.* **A66** 1145
Huber K P and Herzberg G 1979 *Molecular spectra and molecular structure; Constants of diatomic molecules* (New York: Van Nostrand Reinhold Co.) Vol. 4
Hulburt M M and Hirschfelder J O 1941 *J. Chem. Phys.* **9** 61
Joshi K C 1962 *J. Mol. Spectrosc.* **8** 79
Lagerqvist A and Uhler U 1967 *Z. Naturforsch* **B22** 551
Lakshman S V J and Ramakrishna Rao T V 1971 *J. Phys.* **B4** 269
Lakshman S V J and Venkataramanaiah M 1980 *Curr. Sci.* **49** 579
Lefebvre Y and Bocquet J L 1975 *J. Phys.* **B8** 1322
Lefebvre Y and Bocquet J L 1976 *Can. J. Phys.* **54** 1654
Lefebvre Y, Pinchamel B and Bacis R 1976 *Can. J. Phys.* **54** 735
Maheswari R C and Sharma D 1963 *Proc. Phys. Soc.* **81** 898
Nicholls R W and Jarman W R 1956 *Proc. Phys. Soc.* **A69** 253
Thompson K R, Easley W B and Knight L B 1973 *J. Phys. Chem.* **77** 49
Woods L W 1943 *Phy. Rev.* **64** 259