Dissociation energy of CrF molecule

J B Bhartiya

Department of Physics, S B College of Science, Aurangabad-431 001, India

and

S H Behere

Department of Physics, Marathwada University, Aurangabad-431 004, India

Elements in the middle of the periodic table i.e. transition metals yield complex spectra. Naturally, the molecules involving these elements also give complex spectra due to transitions in the electronic states having high multiplicities. Few efforts were made to resolve their spectra and carry out the analysis but they were hardly successful and as a result molecular constants of such molecules were not reported. Diatomic chromium fluoride CrF is an example whose molecular constants are known quite recently.

The spectrum of CrF was reported earlier by Durgavati and Rao (1954). They estimated the ground state frequency around 536 cm^{-1}. Dubov and Shenyavaskaya (1987), recently reinvestigated the CrF molecule in emission as well as in absorption and reported the molecular constants of $A\ ^6\Sigma - X^6\Sigma$ transition. These constants used in present work, are shown in Table 1. They also confirmed the identity of emitter by using various compounds. However, the bands observed by Durgavati and Rao (1954), were not observed by Dubov and Shenyavaskaya (1987). This may be due to the reason that the ground state frequency 662.3 cm^{-1} of CrF reported by Dubov and Shenyavaskaya differs from that of Durgavati and Rao (1954).

The evaluation of dissociation energies of diatomic molecules is of fundamental importance in thermochemistry and astrophysics. Huber and Herzberg (1979) The present investigation deals with the estimation of the value of D_e by fitting the empirical potential function to the Rydberg (1931), Klein (1932), Rees (1947) and Vanderslice.et al (1960) RKRV curve using correlation coefficient method suggested by Rao et al (1981, 1982).

Many empirical potential functions are known for diatomic molecules. Of these, the function given by Hulbert-Hirschfelder (1941, 1961) and Steele and Lippincott (1961), have been used. In the present study, the RKRV curve of the $X^6\Sigma$ state of CrF is constructed using the molecular constants reported by Dubov

6

Table 1. Molecular constants for the ground state x $^6\Sigma$ of CrF (Dubov and Shenyavaskaya, 1987).

ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	B_e (cm^{-1})	α_e^* (cm^{-1})	r_e (Å)
662.3	3.4	0.379	0.002596	1.785

*from Pekeris relation

and Shenyavaskaya (1987). The classical turning points and corresponding U_{RKR} values are presented in Table 2. The H – H potential function which is used to estimate the dissociation energy is of the form

Table 2. Potential energy curves of CrF molecule (turning points).

V	U (cm^{-1})	r_{min} (Å)	r_{max} (Å)
0	330.29	1.728	1.849
1	985.79	1.689	1.900
2	1634.49	1.664	1.938
3	2276.39	1.645	1.970
4	2911.49	1.625	1.999
5	3539.79	1.614	2.026
6	4161.29	1.602	2.051
7	4775.99	1.591	2.075
8	5383.89	1.580	2.099

$$U_{HH}(r) = D_e(8065.48)\{(1-e^{-x})^2 + cx^n e^{-2x}(1+bx)\} \tag{1}$$

where

D_e is in eV.

$$x = [\omega_e/2(8065.48\ B_e D_e)^{\frac{1}{2}}][(r-r_e)/r_e]$$

$$a_0 = \omega_e^2/4B_e\ ;\ a_1 = -1-(\alpha_e\omega_e/6B_e^2)$$

$$a_2 = (5/4)a_1^2 - (2\omega_e x_e/3B_e)$$

$$b = 2 - \{[(7/12)-(8065.48\ D_e).a_o/a_0]/c\}$$

$$c = [1 + a_1(8065.48 D_e.a_2/a_0)^{\frac{1}{2}}]$$

The r_{min} and r_{max} values obtained from RKRV calculations are substituted in eq. (1) and corresponding $U(r)$ values are calculated for different vibrational levels using an

arbitrary value of D_e. These values of $U(r)$ are compared with U_{RKRV} values to obtain a correlation coefficient. In the first stage, D_e values are varied from 1 eV to 6 eV. A good correlation is seen around 4 eV. In order to obtain a better correlation, D_e values are again varied from 3.0 to 4.3 eV in steps of 0.01 and correlation coefficients are obtained for each D_e value. The D_o that corresponds to the maximum correlation coefficient is taken as the best value of D_e.

The values of correlation ceofficients obtained from H — H potential function and RKRV curve are presented in Table 3. It is seen from the table the

Table 3. Correlation between Hulbert-Hirschfelder function and true potential energy curves of CrF-X $^6\Sigma$ state.

D_e (eV)	Correlation coefficient
1	0.9644887
2	0.9988394
3	0.9999492
4	0.9999929
5	0.9999793
6	0.9999711
3.0	0.9999483
3.1	0.9999645
3.2	0.9999746
3.3	0.9999823
3.4	0.9999874
3.5	0.9999915
3.6	0.9999926
3.7	0.9999945
3.8	0.9999942
3.9	0.9999941
4.0	0.9999920
4.1	0.9999915
4.2	0.9999894
4.3	0.9999891

dissociation energy (D_e) obtained in the present work is 3.7 eV for which the maximum correlation coefficient using H — H function is 0.9999945. However, for the same D_e value corresponding value of correlation coefficient using Lippincott potential function is 0.9989134. We conclude that the H — H function gives better fit to RKRV curve of $X^6\Sigma$ state of CrF. The value of $D_e(4.52 \pm 0.20)$ reported earlier by Kent and Margrave (1965), is based on mass spectrometric studies that remained unconfirmed by spectroscopic method. The percentage ionic

character (IC) of CrF is calculated from electronegativities of their constituent atoms, using expressions given by Hannay and Smith (1946), Pauling (1952), Wilmshurst (1959), Batsnov and Durakov (1961) which is presented in Table 4. The average value of IC comes around 58% ; which indicates that the molecule is ionic in nature and

Table 4. Electronegativities and percentage ionic character (IC) for CrF molecule.

$X_A + X_B$	$X_A - X_B$	Hannay and Smyth (1946)	Pauling (1952)	Wilmshurst (1959)	Batsnov and Durakov (1961)
5.6	2.4	58.56	64.54	42.85	68.39

X_A and X_B are electronegativities of the constituent atoms.

hence the ionic binding dominates over covalent binding. The D_0^0 of chromium chloride and bromide are reported by Rao and Rao (1949), Rao (1949) and Bulewicz et al (1961) as 3.7 eV and 3.3 eV respectively. But these thermochemical values are based on flame photometric studies. Since there is no other report of D_0^0 on CrF, for spectroscopic work, the value suggested in present work may be used.

Acknowledgment

References

Batsnov S S and Durakov V I 1961 *J. Struct. Chem.* **2** 424
Bulewicz E M, Phillips J G and Sugden T M 1961 *Transact Faraday Soc.* **57** 921
Dubov V M and Shenyavaskaya E A 1987 *Opt. Spectrosc.* **62** 195
Durgavati B K and Rao V R 1954 *Ind. J. Phys.* **28** 525
Hannay N B and Smyth C B 1946 *J. Am. Chem. Soc.* **68** 171
Huber K P and Herzberg G 1979 *Constants of Diatomic Molecules.* (New York : Van Nostrand Reinhold Company)
Hulbert H M and Hirschfelder J O 1941 *J. Chem. Phys.* **9** 61
——1961 *J. Chem. Phys.* **35** 1901
Kent F and Margrave J L 1965 *J. Am. Chem. Soc.* **87** 3582
Klein O 1932 *Z. Phys.* **76** 226
Pauling L 1952 *J. Phys. Chem.* **56** 361
Rao V R and Rao K R 1949 *Ind. J. Phys.* **23** 508
Rao V R 1949 *Curr. Sci.* **18** 338
Rao V M, Rao M L P and Rao P T 1981 J. Quant. Spectrosc Radiat. Transfer **25** 547
——1982 *Phys. Rev.* **A 26** 1765
Rees A L G 1947 *Proc. Phys. Soc.* **59** 998
Rydberg R 1931 *Z. Phys.* **73** 376
Steele D and Lippincott E R 1961 *J. Chem. Phys.* **35** 2065
Vanderslice J A, Mason E A, Maisch W G and Lippincott E R 1960 *J. Mol. Spectrosc.* **5** 83
Wilmshurst J K 1959 *J. Chem. Phys.* **30** 561