

Dissociation energy of CO^+ from the true potential energy curve

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Abstract. The dissociation energy for the ground state of CO^+ has been estimated to be 9.30 ± 0.35 eV by the method of curve fitting. The three parameter Lippincott potential function has been used for fitting with the RKR curve.

Keywords. Dissociation energy; Lippincott potential function; RKR curve; CO^+ .

1. Introduction

The most prominent bands in the spectra occurring in the tail of the comet are the ${}^2\Pi - {}^2\Sigma$ bands of CO^+ which are named as 'the comet tail bands' (Herzberg 1950). Spectroscopic investigations on CO^+ are necessary for an understanding of the physical features of the comet. Gaydon (1968) has pointed out that a knowledge of the exact value of the dissociation energy of diatomic molecules is of fundamental importance for thermochemistry and it is often of interest in astrophysics. Biskamp (1933) has given a value of $D_e = 9.9$ eV for the dissociation energy of the ground state of CO^+ by using the linear extrapolation technique. Asundi (1943) has reported a value $D_0 = 9.9$ eV obtained from spectroscopic data and the value $D_0 = 9.2$ eV as deduced from collision data. Gaydon (1968) has proposed a value of 8.34 eV given by Brewer and Searcy (1956), as the most probable value of D_0 for the ground state of CO^+ . The present investigation deals with the estimation of the value of D_e by the method of curve fitting using the true potential energy curve and the molecular constants reported by Biskamp (1933) and Rao (1950).

2. The RKR turning points

The turning points for the ground state of CO^+ are calculated according to the RKR procedure as extended by Vanderslice *et al* (1960), using the experimental data for all the observed vibrational levels, in the expression

$$r_{\max, \min} = [(f/g) + f^2]^{1/2} \pm f. \quad (1)$$

Simplified expressions are used for the evaluation of f and g as given by Singh and Jain (1962) (Murthy and Murthy 1970). The RKR turning points for the ground state of CO^+ are given in table 1 together with those obtained by using the Morse

Table 1. Turning points of the vibrational motion

v	$G(v)$ cm^{-1}	RKR V		Morse	
		$r_{\text{max}} \text{ \AA}$	$r_{\text{min}} \text{ \AA}$	$r_{\text{max}} \text{ \AA}$	$r_{\text{min}} \text{ \AA}$
0	1103.33	1.165	1.071	1.165	1.071
1	3287.24	1.206	1.041	1.206	1.041
2	5440.83	1.236	1.022	1.236	1.022
3	7564.11	1.262	1.008	1.262	1.008
4	9657.07	1.286	0.996	1.286	0.996
5	11719.72	1.308	0.985	1.308	0.985
6	13752.07	1.329	0.976	1.329	0.976
7	15754.11	1.350	0.968	1.350	0.968
8	17725.87	1.370	0.961	1.370	0.961
9	19667.32	1.389	0.954	1.389	0.954
10	21578.50	1.408	0.947	1.408	0.947
11	23459.38	1.427	0.941	1.427	0.942
12	25309.98	1.445	0.936	1.445	0.936
13	27130.32	1.463	0.931	1.464	0.932
\vdots	\vdots	\vdots	\vdots	\vdots	\vdots
72	80847.65	5.103	0.576	5.363	0.836

(1929) potential function for comparison. The turning points and the extrapolated energy value for the highest bound level in the Morse potential have been indicated. The table also contains the energy values $G(v)$ obtained from the experimental data.

3. The method of curve fitting

An accurate estimation of the dissociation energy by the method of curve fitting requires an empirical potential function which gives the best reproduction of the true potential energy curve. In the present investigation the Lippincott potential function in the original form (Steele and Lippincott 1961) has been chosen as the empirical function since it has been shown to fit well with the RKR V curves of a large number of molecules (Steele *et al* 1962) and it is given by the expression

$$U(r) = D_e \left[1 - \exp \left\{ -\frac{n(r-r_e)^2}{2r} \right\} \right] \left[1 - a \left(\frac{b^2 n}{2r} \right)^{1/2} (r-r_e) \right. \\ \left. \exp \left\{ -\left(\frac{b^2 n r_e}{2r} \right)^{1/2} (r-r_e) \right\} \right] \quad (2)$$

$$\text{where } a = \frac{4}{5} \left(1 - \frac{1}{b \Delta^{1/2}} \right), \quad \Delta = \frac{k_e r_e^2}{2D_e}, \quad n = \frac{2\Delta}{r_e}$$

$$\text{and } b = 1.065.$$

The RKR V turning points are used in the above expression and for a particular value of D_e , the energy values $U(r)$ are compared with $G(v)$. This is repeated for different values of D_e in steps of 0.05 eV and the value for which the best fitting of

Table 2. Comparison of the observed and calculated energy values

$r\text{\AA}$	$G(v)$ cm^{-1}	$D_e = 9.25 \text{ eV}$		$D_e = 9.30 \text{ eV}$		$D_e = 9.35 \text{ eV}$	
		$\bar{U}(r)$ cm^{-1}	% deviation	$\bar{U}(r)$ cm^{-1}	% deviation	$\bar{U}(r)$ cm^{-1}	% deviation
1.165	1103.33	1107.20	0.35	1107.52	0.38	1107.84	0.41
1.206	3287.24	3315.79	0.87	3317.52	0.92	3319.24	0.97
1.236	5440.83	5501.74	1.12	5505.56	1.19	5509.36	1.26
1.262	7564.11	7657.96	1.24	7664.43	1.32	7670.84	1.41
1.286	9657.07	9779.99	1.27	9789.60	1.37	9799.15	1.47
1.308	11719.72	11863.24	1.23	11876.44	1.34	11889.55	1.44
1.329	13752.07	13906.48	1.12	13923.70	1.25	13940.80	1.37
1.350	15754.11	15907.29	0.97	15928.92	1.11	15950.42	1.24
1.370	17725.87	17861.47	0.77	17887.90	0.91	17914.16	1.06
1.389	19667.32	19767.10	0.51	19798.67	0.66	19830.04	0.83
1.408	21578.50	21624.74	0.21	21661.80	0.39	21698.63	0.56
1.427	23459.38	23433.20	0.11	23476.06	0.07	23518.66	0.25
1.445	25309.98	25188.33	0.48	25237.28	0.28	25285.93	0.09
1.463	27130.32	26888.11	0.89	26943.43	0.68	26998.41	0.49
1.071	1103.33	1100.32	0.27	1100.02	0.30	1099.72	0.32
1.041	3287.24	3268.25	0.58	3266.75	0.62	3265.25	0.67
1.022	5440.83	5405.61	0.65	5402.42	0.70	5399.26	0.76
1.008	7564.11	7516.94	0.62	7511.73	0.69	7506.57	0.76
0.996	9657.07	9605.16	0.54	9597.66	0.61	9590.23	0.69
0.985	11719.72	11672.04	0.41	11662.02	0.49	11652.11	0.57
0.976	13752.07	13718.11	0.25	13705.37	0.34	13692.77	0.43
0.968	15754.11	15745.99	0.05	15730.37	0.15	15714.89	0.25
0.961	17725.87	17754.35	0.16	17735.68	0.06	17717.20	0.05
0.954	19667.32	19748.05	0.41	19726.18	0.29	19704.55	0.19
0.947	21578.50	21722.31	0.67	21697.14	0.55	21672.23	0.43
0.941	23459.38	23682.93	0.95	23654.32	0.83	23626.00	0.71
0.936	25309.98	25677.07	1.25	25594.95	1.12	25563.11	1.00
0.931	27130.32	27564.07	1.60	27528.29	1.47	27492.82	1.33
Average % deviation			0.70		0.68		0.75

the energy values is achieved is taken to be the dissociation energy of the molecule for the state considered. Such a procedure has been employed for the ground states of BeO (Murthy and Prahlad 1977), AlO (Murthy *et al* 1977) and MgO (Murthy and Bagare 1977). The calculations have been carried out for values of D_e ranging from 8.5 eV to 9.9 eV and only the results which are necessary for comparison are given in table 2 for the ground state of CO^+ . The calculations involved in the present investigation were carried out using the computer IBM 360 at the Indian Institute of Science, Bangalore.

4. Results and discussion

Table 1 shows that the RKR turning points agree well with those of Morse even for higher vibrational levels as the deviation in the value of α_e calculated using the Pekeris relation (0.01874 cm^{-1}) from the experimental value (0.019 cm^{-1}) is very small (Murthy and Murthy 1970).

It is evident from table 2 that the best fitting of the energy values is achieved for $D_e = 9.30$ eV since the average percentage deviation in this case is minimum. Hence the dissociation energy for the ground state of CO^+ is 9.30 ± 0.35 eV and the value as measured from the lowest vibrational level is $D_0 = 9.16$ eV. This value of D_0 is significant because it has been estimated by using the true potential energy curves based on experimental data. It is very near to the value ($D_0 = 9.2$ eV) obtained by Asundi (1943) from the collision data.

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