DISSOCIATION ENERGIES OF DIATOMIC MOLECULES FROM VIBRATIONAL SPACINGS OF HIGHER LEVELS: APPLICATION TO THE HALOGENS *

ROBERT J. LEROY ** and RICHARD B. BERNSTEIN
Theoretical Chemistry Institute and Chemistry Department, University of Wisconsin, Madison, Wisconsin 53706, USA

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The distribution of vibrational levels near the dissociation limit D, governed mainly by the long-range part of the potential, can be WKB-approximated to yield a simple expression which permits accurate determination of D. Improved ground-state dissociation energies are presented for Cl_2, Br_2 and I_2.

1. INTRODUCTION

Since its introduction 44 years ago, the Birge–Sponer (BS) extrapolation procedure has been widely used (mostly in its original form) to evaluate dissociation limits (D) of diatomic molecules from vibrational spectroscopic data [1]. The main difficulty in its application arises from the curvature generally exhibited in the "tails" of BS plots near the dissociation limit, which give rise to uncertainty in the extrapolation. The present communication reports a better, WKB-based method (derived and more fully discussed elsewhere [2]) which takes proper account of this curvature.

The new procedure has been applied to the halogens [2], yielding ground state D_0 values with much smaller uncertainties than heretofore obtainable. These results are presented in section 3.

2. METHOD

For highly excited vibrational levels lying close to the dissociation limit D, the potential $V(R)$ through their outer turning points may be well represented by an inverse-power functionality

$$V(R) = D - C_n/R^n. \tag{1}$$

Differentiating the WKB eigenvalue expression with respect to energy, approximating the exact potential by eq. (1), and integrating (neglecting the small contribution to the exact integral from the region of the inner turning point), one obtains

$$\frac{dE(v)}{dv} = \hbar\sqrt{\frac{2\pi}{\mu}}\,\frac{\Gamma\left(1+\frac{1}{n}\right)}{\Gamma\left(\frac{1}{2}+\frac{1}{n}\right)}\,\frac{n}{C_n^{1/n}}\,[D-E(v)]^{\left(\frac{n+2}{2n}\right)}$$

$$= K_n[D-E(v)]^{\left(\frac{n+2}{2n}\right)}. \tag{2}$$

Here $E(v)$ is the rotationless ($J=0$) energy of level v, μ the reduced mass, $\Gamma(x)$ the gamma function, and K_n a collection of constants; $dE(v+\frac{1}{2})/dv$ is very nearly $\Delta G_{v+\frac{1}{2}}$, the conventional BS ordinate. Eq. (2) requires (as is generally observed) positive (upward) curvature in BS plots for energies near enough to the dissociation limit for eq. (1) to be appropriate.

In practical applications it is convenient to use the integrated form of eq. (2); for $n \neq 2$ this becomes‡

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‡ Expressions analogous to eq. (3) have also been obtained [2,3] for the $n = 2$ case, and for a potential with an exponential long-range tail.

$$E(v) = D - [(v_D - v)H_n]^{\left(\frac{2n}{n-2}\right)}, \qquad (3)$$

where

$$H_n \equiv \left(\frac{n-2}{2n}\right) K_n \ .$$

Here v_D is an integration constant; for cases of $n > 2$ it can be identified as the "effective" (non-integer) vibrational index at the dissociation limit (i.e., $E(v_D) = D$).

Determination of D (together with n, C_n, and v_D) using eq. (3) requires at least four (preferably more) vibrational energies. The best approach is to carry out a non-linear least-squares fit of experimental eigenvalues to eq. (3), to yield a "best" set of parameters. However, typical non-linear regression programs* require fairly accurate initial trial values of the unknowns to ensure convergence to the "best" final values. Suitable starting values for n and v_D may be obtained by fitting the data to the following *linear* expression, obtained from eq. (3):

$$\frac{dE(v)/dv}{d^2E(v)/dv^2} = -\left(\frac{n-2}{n+2}\right)(v_D - v) \ . \qquad (4)$$

Using these n and v_D values, eq. (3) becomes linear in the new variable

$$w \equiv \left[\left(\frac{n-2}{2n}\right)(v_D - v)\right]^{\left(\frac{2n}{n-2}\right)},$$

$$E(v) = D - wK_n^{\left(\frac{2n}{n-2}\right)}, \qquad (3')$$

Fitting the data to eq. (3') then yields trial values of D and K_n. The full set of parameters now serves as the trial set for the refined non-linear least-squares fit to eq. (3) which yields the "best" parameter values. In principle, eqs. (4) and (3') are just as accurate as eq. (3). However, in practice, the prior smoothing of experimental energies to obtain the derivatives in eq. (4) introduces some error, so that the subsequent fit to eq. (3) is slightly more reliable.

3. RESULTS. GROUND-STATE DISSOCIATION ENERGIES OF THE HALOGENS

Application of the present method to spectroscopic data for Cl_2, Br_2, and I_2, together with conclusions regarding the nature of the long-range forces, are discussed in detail elsewhere [2,3]. Attention here is restricted to the values obtained for the ground ($X\,^1\Sigma_g^+$) state dissociation energies.

The experimental data are the band origins for transitions between the $v'' = 0$ level of the ground electronic state and highly excited vibrational levels (v') of the $B\,^3\Pi_{0u}^+$ state. Fitting these to eq. (3) by the numerical methods discussed in section 2, yielded the dissociation limits D for the B-states. Subtracting from D the accurately known $^2P_{1/2}$ - $^2P_{3/2}$ atomic spin-orbit splitting (ΔE) yielded values of D_0 for the ground ($X\,^1\Sigma_g^+$) states.

3.1. *Chlorine*

The most extensive measurements are for $^{35,35}Cl_2$ [4]. The present analysis of these data places D some 2.85(±0.15) cm^{-1} above the highest observed level, $v' = 31$ (cf. the experimenters' value: 3.1(±2) cm^{-1} [4]. Subtracting from D the ΔE of 882.50 cm^{-1} [5,6] yields a dissociation energy of D_0 = 19 997.25(±0.15) cm^{-1} (see table 1).

3.2. *Bromine*

For each of the pure isotopic species $^{79,79}Br_2$ and $^{81,81}Br_2$, energies of four adjacent vibrational levels very near the B-state dissociation limits have been reported [7]. Analysis by the present method yielded binding energies of 5.24(±0.17) cm^{-1} and 6.96(±0.22) cm^{-1}, respectively, for the highest observed level of each species, $v' = 53$‡.

‡ It has been found [3] that the experimenters' [7] vibrational assignments for the four levels near the dissociation limit should be increased by one.

Table 1
Results for the halogens[a)]

Species	v'_H	$B\,^3\Pi_{0u}^+$ state $D - E(v'_H)$ (cm^{-1})	$X\,^1\Sigma_g^+$ state D_0 (eV)
$^{35,35}Cl_2$	31	2.85 ± 0.15 (3.1 ± 2.0) [4]	2.479 367 ± 0.000 019
$^{79,79}Br_2$	53	5.24 ± 0.17 (2.7 ± 0.5) [7]	1.970 69 ± 0.000 04
$^{81,81}Br_2$	53	6.96 ± 0.22 (4.1 ± 0.5) [7]	1.970 95 ± 0.000 05
$^{127,127}I_2$	72	19.6 ± 1.1 (12.6) [9]	1.542 49 ± 0.000 14

a) The values in parentheses are the previous best estimates of these binding energies. The uncertainties in the present results correspond to a 95% statistical confidence limit. The energy conversion factor was taken from ref. [16].

* The present computations employed the University of Wisconsin Computing Center's subroutine GASAUS.

These values are significantly greater than the 2.7(± 0.5) and 4.1(± 0.5) cm^{-1}, respectively, obtained [7] from extrapolations of limiting curves of dissociation. Subtracting ΔE = = 3685.2(± 0.3) cm^{-1} [8] from the thus-obtained D values yields:

$$D_0(^{79,79}Br_2) = 15\,894.5(\pm 0.3_4)\ cm^{-1},$$

and

$$D_0(^{81,81}Br_2) = 15\,896.6(\pm 0.3_7)\ cm^{-1}.$$

The zero-point shift is in good accord with the more-directly obtained value of 2.029(± 0.013) cm^{-1} from ref. [7].

3.3. *Iodine*

For the case of $^{127,127}I_2$, the data [9] for the highest observed levels of the B-state are relatively less accurate. The present analysis yields a binding energy for the uppermost recorded level, $v' = 72$*, of 19.6(± 1.1) cm^{-1} (considerably greater than the experimenter's estimate [9] of 12.6 cm^{-1}).

Using ΔE = 7603.15 cm^{-1} [5,12] one obtains D_0 = 12 440.9(± 1.1) cm^{-1}. This value differs significantly with the previously recommended one of 12 452.5(± 1.5) cm^{-1} [13]; the source of the discrepancy is discussed elsewhere [14].

4. CONCLUSIONS

A new method has been described for extrapolating beyond the highest observed vibrational levels of a diatomic molecule to determine its dissociation limit. On the basis of the available evidence [2,3], it appears to be more reliable than the utilization either of the limiting curve of dissociation** or of a BS extrapolation. For levels near the dissociation limit for which the BS plot shows positive curvature, its use should supersede that of the conventional Birge–Sponer extrapolation.

Table 1 summarizes the results of applying the present method to the determination of the halogen dissociation energies. Binding energies of the highest observed B-state vibrational levels (v'_H) are also tabulated and compared with previously reported values.

*It has been found [10,11] that the vibrational numbering of ref. [9] should be decreased by one.

**See, for example, ref. [15].

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