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Improved Spectroscopic Dissociation Energy for Ground-State Ar₂

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Tanaka and Yoshino¹ recently observed a number of vibrational bands in the vacuum uv absorption spectrum of ground-state O_g⁺(¹Σ_g⁺)Ar₂. They obtained an estimate of $D_0 = 76.9 (\pm 1.9) \text{ cm}^{-1}$ for the molecular dissociation energy from a linear extrapolation of a Birge-Sponer plot of their vibrational spacings. In addition, they concluded that the six vibrational levels they observed are all that this potential well holds.² Presented here is a re-analysis of their data which yields both a considerably improved experimental dissociation energy of $D_0 = 84.0 (\pm 3.5) \text{ cm}^{-1}$ (or $D_e = 98.7 (\pm 3.5) \text{ cm}^{-1}$) and the energies of three additional unobserved levels ($v = 6-8$). It is based on the known form³ of the distribution of vibrational levels near dissociation where the outer branch of the potential takes on its theoretical asymptotic form, $V(R) = D - C_n/R^n$. In this case the level energies are given by

$$G(v) = D - [(v_D - v)H_n]^{2n/(n-2)}, \quad (1)$$

where D is the dissociation limit, v_D the vibrational index at D , and $H_n \equiv H_n/[\mu^{1/2}(C_n)^{1/n}]$, with μ being the diatomic reduced mass and \tilde{H}_n being a numerical constant depending only on n .³

Before proceeding with the application of Eq. (1) we must first ask whether it is valid for the Tanaka-Yoshino data.¹ The long-range potential of ground-state Ar₂ is given by

$$V(R) = D - C_6/R^6 - C_8/R^8 - \dots, \quad (2)$$

where $C_6 = 3.26 (\pm 0.10) \times 10^5 \text{ cm}^{-1} \text{ \AA}^6$,⁴ and $C_8 = 1.52 (\pm 0.18) \times 10^6 \text{ cm}^{-1} \text{ \AA}^8$.⁵ For $R > 5 \text{ \AA}$ the second (R^{-8}) term in Eq. (2) is clearly only a small fraction of the magnitude of the leading (R^{-6}) term. Furthermore, it seems unlikely that charge overlap and exchange effects will be strong in this region,⁶ particularly in view of the closed-shell electronic structure of Ar.

Therefore, the potential at $R \gtrsim 5.5 \text{ \AA}$ should be dominated by the leading (R^{-6}) term in Eq. (2). The Morse potential which Tanaka and Yoshino¹ constructed from their data shows that the outer turning points of levels $v \geq 4$ lie in this region,⁷ and hence that their eigenvalues should be accurately described by Eq. (1) with $n = 6$.

For each of $v = 0-3$, all the separate measurements¹ of the vibrational spacing $\Delta G_{v+1/2}$ were averaged to give the values (and standard errors) shown in Fig. 1.² The round points associated with the left ordinate scale correspond to a standard Birge-Sponer plot, and the Line E is the experimenters'¹ linear extrapolation of it to obtain their D_0 . On the other hand, differentiating Eq. (1), setting $n = 6$, and approximating

$$[dG(v + \frac{1}{2})/dv] \approx \Delta G_{v+1/2},$$

one obtains

$$(\Delta G_{v+1/2})^{1/2} = [3(H_6)^3]^{1/2}(v_D - v - \frac{1}{2}), \quad (3)$$

where the known⁴ C_6 yields $H_6 = 0.5377 (\pm 0.0026)$. The triangular points associated with the right ordinate scale in Fig. 1 show the plot suggested by Eq. (3), and the line T is a linear extrapolation of these points using the theoretical slope $[3(H_6)^3]^{1/2}$. The two dashed lines are extreme upper and lower bounds associated with the uncertainties in H_6 and $\Delta G_{7/2} = 10.62 (\pm 0.79) \text{ cm}^{-1}$. Substituting the resulting $v_D = 8.27 (\pm 0.21)$ into Eq. (1) with $n = 6$ and the known H_6 , then yields binding energies $[D - G(v)]$ of 12.1 (± 1.7), 5.4 (± 1.0), 1.8 (± 0.5), 0.32 (± 0.15), and 0.003 ($+0.014, -0.003$) cm^{-1} for $v = 4-8$, respectively. Analogously, upper bounds to the rotational constant B_v for these levels are given by $B_v(\text{upper}) = 0.0107(v_D - v)$.⁸ Adding the calculated binding energy for $v = 4$ to the experimental vibrational spacings yields an improved ground-state

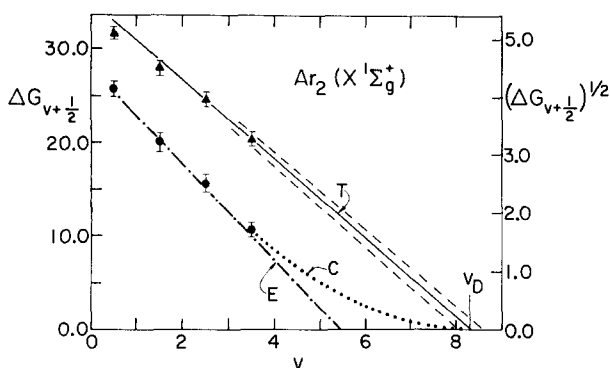


FIG. 1. Plot of experimental vibrational spacings (in cm^{-1})¹ vs vibrational quantum number. Left ordinate scale: points ●, Line E and Curve C; right ordinate scale: points ▲ and Line T.

Ar_2 dissociation energy of $D_0 = 84.0 (\pm 3.5) \text{ cm}^{-1}$.⁹ Combined with Tanaka and Yoshino's¹ vibrational constants this corresponds to $D_0 = 98.7 (\pm 3.5) \text{ cm}^{-1}$.⁹

It should be noted that the potential well depth obtained here is in excellent agreement with both the 98.76 cm^{-1} of the current best semi-empirical potential¹⁰ and the 99.04 cm^{-1} obtained on adding a vibrational amplitude correction to an earlier bulk-properties potential.¹¹ It is also in good accord with the values $102.2 (\pm 2.)$, 100.4 , and 97.81 cm^{-1} obtained from recent molecular beam scattering measurements.^{12,13} As with the best of the earlier Ar_2 potentials,^{14,15} these empirical curves all have vibrational spacings in reasonable agreement with experiment.

The contrast in Fig. 1 between the correct Birge-Sponer extrapolation, Curve C, and the experimenters'¹ linear extrapolation (labeled E) dramatically demonstrates the importance of utilizing Eq. (1) when discussing the convergence of vibration levels to dissocia-

tion. The fact that the original estimate¹ of the total number of vibrational levels appears to be 50% too small also emphasizes the influence of long-range forces on the total number of levels bound by a potential.¹⁶

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² The highest observed level $v=5$ appeared in only one of the several series of bands, and its relative position (i.e., $\Delta G_{v/2}$) was not tabulated for this case.¹ Hence, the present analysis uses only the $v \leq 4$ data.

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Relationship between Self-Diffusion Coefficients and Interdiffusion Coefficients in Carbon Tetrachloride-Cyclohexane and Acetone-Water Systems

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The relationship between the self-diffusion coefficients of the components and the interdiffusion coefficient for a binary system has been described by Darken¹ and by Hartley and Crank² as Eq. (1):

$$\bar{D} = (N_1 D_2^* + N_2 D_1^*) d \ln a_1 / d \ln N_1, \quad (1)$$

where \bar{D} is the interdiffusion coefficient, D^* the self-

diffusion coefficient, N the mole fraction, a the activity, and the subscript i refers to component i . In the present work, the validity of Eq. (1) was tested for two binary systems of organic liquids by comparing the interdiffusion coefficient experimentally determined and that theoretically calculated with Eq. (1). Tested were the carbon tetrachloride-cyclohexane and acetone-