Reexamination of the I_2 Spectrum near the $B(^3\Pi_{0u}^+)$ State Dissociation Limit

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The disagreement of Danyluk and King's (*Chem. Phys.* **25**, 343 (1977)) rotational constants for levels lying near the dissociation limit of B-state I_2 with the mechanical behavior predicted by near-dissociation theory is investigated. The discrepancies are shown to be much too large to be explained by either the neglect of centrifugal distortion effects in the original analysis or by rotational or spin–rotation coupling to a nearby repulsive 1_u state. These differences are therefore attributed to experimental error, a conclusion which is confirmed by more recent experimental results. A reanalysis of the best available data for levels near the dissociation limit of B-state I_2 then yields improved values for the B-state dissociation limit $\mathcal{D} = 20\ 043.16\ (\pm 0.02)$ cm^{-1} of the vibrational index at dissociation $v_\mathcal{D} = 87.32\ (\pm 0.04)$ and of the long-range potential constant $C_5 = 2.88\ (\pm 0.03) \times 10^5\ cm^{-1}\ \text{Å}^5$. This in turn implies a slightly improved ground-state dissociation energy of $\mathcal{D}_0 = 12\ 440.18\ (\pm 0.02)\ cm^{-1}$.

I. INTRODUCTION

Although it is one of the most thoroughly studied species in all of molecular spectroscopy, the $B(^3\Pi_{0u}^+)$ state of I_2 is a continuing source of new puzzles. The present work addresses one of these, the discrepancies between reported experimental rotational constants for the highest observed vibrational levels of this state (*1*) and the predicted mechanical behavior of these constants for levels approaching dissociation (*2–4*). In the course of resolving this disagreement, the present paper also instructively illustrates the utility of some recently developed theoretical tools of molecular spectroscopy.

Using their technique of two-photon sequential absorption spectroscopy, Danyluk and King (*1*) observed transitions involving some of the most weakly bound vibrational levels of B-state I_2. On applying limiting near-dissociation theory (*5*) to their vibrational energies for $v = 77$–82 and those of Barrow and Yee (*6*) for $v = 70$–77, they obtained estimates of the dissociation energy $\mathcal{D}$, the vibrational index at dissociation $v_\mathcal{D}$, and the long-range potential energy coefficient C_5. With this infor-

mation, the limiting near-dissociation expressions for the vibrational energy derivative ω_v^∞ and the rotational constant B_v^∞ are (2, 5)

$$\omega_v^\infty = 0.00711(v_\mathcal{D} - v)^{7/3} \tag{1}$$

$$B_v^\infty = 0.000274(v_\mathcal{D} - v)^{4/3}. \tag{2}$$

The points in Fig. 1 compare the predictions of Eqs. (1) and (2) with the experimental results of Luc (7), Barrow and Yee (6), and Danyluk and King (1), while the curves indicate the predicted mechanical behavior of these quantities for levels approaching dissociation. In this context, a level is said to exhibit "mechanical behavior" if its eigenvalue and other properties are determined by a solution of the radial Schrödinger equation for some given potential energy curve. It is therefore clear that the curves in Fig. 1 must approach unity as $v \rightarrow v_\mathcal{D}$. The curves shown are based on near-dissociation expansion fits (4, 8) to Luc's (7) experimental data for $v = 1$–62; they are clearly in excellent agreement with the Barrow and Yee (6) results for $v = 63$–77 and with the vibrational energy derivatives of Danyluk and King (1), at least up to $v = 78$. However, the Danyluk and King rotational constants deviate markedly from these predictions for $v > 78$. Since the near-dissociation expansion predictions are in very good agreement with values calculated from an RKR potential for this state (see below), it seems clear that Danyluk and King's (1) B_v constants for their highest observed levels are inconsistent with a mechanical description of this state. The second and third columns of Table I compare the predicted "mechanical" constants B_v(mech) with experiment B_v(obs); the differences between these quantities, listed in the fourth column of Table I, are the discrepancies with which the present paper is concerned.
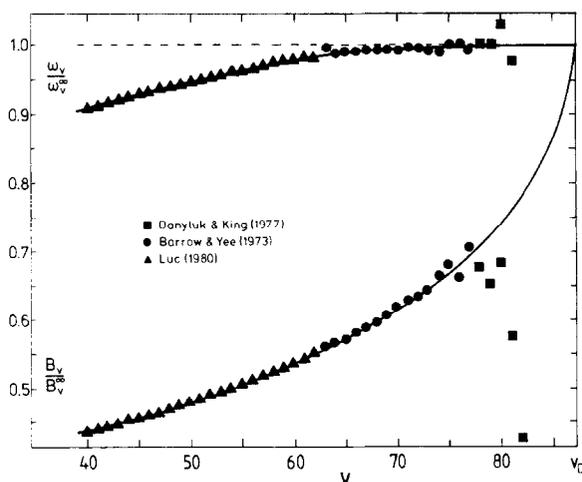
FIG. 1. Comparison of experimental vibrational energy derivative ω_v and rotational constant B_v with their predicted limiting near-dissociation behavior. Points represent experimental data, while the solid curves represent "mechanical" values generated from near-dissociation expansion fits to the data for levels $v = 1$–62.

When these differences were first noticed, they were attributed to neglect of centrifugal distortion constants in the experimentalists' rotational analysis (*3*). However, plots of rotational term values vs $\mathcal{J}(\mathcal{J} + 1)$ show no obvious curvature, and fits to the Danyluk–King term values while holding the centrifugal distortion constants fixed at values predicted by the near-dissociation expansion expressions of Ref. (*4*) yielded $G(v)$ and B_v values which differed only slightly from those originally reported. Thus, the discrepancies in question are not due to neglect of centrifugal distortion effects.

A promising alternate explanation of this problem was provided by Cummings' prediction that a heterogeneous rotational perturbation by one of the two nonbonding 1_u states with the same dissociation limit as the $B(0_u^+)$ state will cause the effective B_v values to be smaller than the mechanical values implied by the B-state potential energy curve (*9*). He also pointed out that this effect would only be noticeable for levels near dissociation whose outer turning points lie at long range where the potential curves are close to one another.

The rotational perturbation mechanism and the effect of spin–rotation coupling are discussed in the next two sections. However, it is shown there that these perturbations are much too small to explain the observed discrepancies. As a result, it appears that these discrepancies must be attributed to errors in the experimental results. For $v = 78$–80 this conclusion is confirmed by recent experimental work of Gerstenkorn and Luc (*10*). These new data are presented in Section IV, together with a reexamination of the nature of the two-photon sequential absorption experiment. A reanalysis of the best available data for this species is then used to obtain improved values of the limiting near-dissociation theory constants for this system.

II. CORIOLIS (OR ROTATIONAL) COUPLING HYPOTHESIS

A. Theory

For present purposes, the Hamiltonian for a freely rotating and vibrating diatomic molecule may be written as (*11*)

$$H = H_0 + H_R + H_{fs}$$

TABLE I

Comparison of Observed and "Mechanical" Rotational Constants (in cm^{-1}) for B-State I_2, with the Predicted Coriolis Coupling Perturbation Constant $\Delta B(R^*)$

v	B_v(obs)	B_v(mech)	$[B_v$(mech)$-B_v$(obs)]	D_v(mech)	$\Delta B_v(R^*)$		
					$R^* = \infty$	$R^* = 11$	$R^* = 7$
75	-------	51.33×10^{-4}	------	0.0021×10^{-4}	0.110×10^{-4}	0.122×10^{-4}	0.128×10^{-4}
78	$35.77(\pm 1.00) \times 10^{-4}$	37.31×10^{-4}	$1.54(\pm 1.00) \times 10^{-4}$	0.0032×10^{-4}	0.150×10^{-4}	0.158×10^{-4}	0.160×10^{-4}
79	$29.64(\pm 1.25) \times 10^{-4}$	32.70×10^{-4}	$3.06(\pm 1.25) \times 10^{-4}$	0.0037×10^{-4}	0.170×10^{-4}	0.170×10^{-4}	0.174×10^{-4}
80	$25.91(\pm 1.43) \times 10^{-4}$	28.13×10^{-4}	$2.22(\pm 1.43) \times 10^{-4}$	0.0044×10^{-4}	0.192×10^{-4}	0.192×10^{-4}	0.190×10^{-4}
81	$17.84(\pm 0.80) \times 10^{-4}$	23.63×10^{-4}	$5.79(\pm 0.80) \times 10^{-4}$	0.0053×10^{-4}	0.220×10^{-4}	0.210×10^{-4}	0.210×10^{-4}
82	$10.64(\pm 4.13) \times 10^{-4}$	19.20×10^{-4}	$8.56(\pm 4.13) \times 10^{-4}$	0.0066×10^{-4}	0.258×10^{-4}	0.236×10^{-4}	0.236×10^{-4}

where H_0 is the Hamiltonian for a nonrotating molecule, H_{fs} is the fine structure Hamiltonian (to be discussed in Section III), and H_R is the nuclear rotation operator

$$H_R = (\hbar^2/2\mu R^2)\mathcal{R}^2 = (\hbar^2/2\mu R^2)(\mathcal{J} - J)^2$$

where $\mathcal{R}$ is the nuclear rotation angular momentum operator and $\mathcal{J}$ and J are the total and electronic angular momentum operators, respectively. Within the adiabatic approximation (*12*), each eigenfunction of H_0 is a product of nuclear and electronic motion wave functions which have no nonzero off-diagonal matrix elements with the spin–orbit coupling operator.

Cummings (*9*) showed that the matrix element of H_R between the $0_u^+(B^3\Pi)$ state and one of the two 1_u states with the same $(^2P_{3/2} + {}^2P_{1/2})$ dissociation threshold will be nonzero. Since Mulliken (*13*) had shown that both of these 1_u states are strongly repulsive, Cummings also concluded that the resulting heterogeneous rotational perturbation would compress the rotational structure and cause the empirical B_v values to be smaller than would be predicted by a simple mechanical model. Because of the energy denominator factor appearing in the normal expression for second-order perturbation energies, he also noted that this effect should only be noticeable for vibrational levels lying very close to dissociation.

In Cummings' analysis (*9*), the eigenfunctions of H_0 are written as

$$\Psi_{\beta v}(\mathbf{r}, R) = \Phi_{\beta J\Omega}(R; \mathbf{r})\chi_{\beta v}(R) \tag{3}$$

where $\mathbf{r}$ denotes the electronic coordinates, $\Phi_{\beta J\Omega}(R; \mathbf{r})$ is the electronic wave function for electronic state β, J the total electronic angular momentum quantum number, Ω the quantum number associated with the projection of the total electronic angular momentum onto the internuclear axis, and $\chi_{\beta v}(R)$ the radial wave function for vibrational level v. In this basis, the matrix elements of H_R are zero unless $\Delta J = 0$ and $\Delta\Omega = 0, \pm 1$. The resulting diagonal (in J and Ω) electronic matrix elements have the form

$$H_{\beta\beta'}(R) = \langle \Phi_{\beta J\Omega}(R; r)|H_R|\Phi_{\beta'J\Omega}(R; \mathbf{r})\rangle$$

$$= B(R)[\mathcal{J}(\mathcal{J} + 1) + J(J + 1) - 2\Omega^2] \tag{4}$$

where $B(R) = \hbar^2/2\mu R^2$. If $\beta = \beta'$ this (scalar) radial operator yields the usual perturbation theory expression for the rotational and centrifugal distortion constants (*14,15*).

At the separated atom limit for *B*-state I$_2$, $J = 2$ and $\Omega = 0$ (*9*), so Eq. (4) yields the rotational energy level expression

$$E(v, J) = G(v) + B_v[\mathcal{J}(\mathcal{J} + 1) + 6] + D_v[\mathcal{J}(\mathcal{J} + 1) + 6]^2 + \cdots$$

$$= \{G(v) + 6B_v - 36D_v + \cdots\} + [\mathcal{J}(\mathcal{J} + 1)]\{B_v - 12D_v$$

$$+ 108H_v + \cdots\} - [\mathcal{J}(\mathcal{J} + 1)]^2\{D_v - 18H_v + \cdots\} + \cdots]. \tag{5}$$

Thus, even in the absence of off-diagonal coupling terms, the effective rotational and centrifugal distortion constants, defined as the coefficients of powers of $[\mathcal{J}(\mathcal{J} + 1)]$ determined from fits to Eq. (5), will differ from their mechanical values; in particular,

$$B_v(\text{eff}) = B_v(\text{mech}) - 12D_v(\text{mech}) + 108H_v(\text{mech}) + \cdots. \tag{6}$$

As $v \rightarrow v_{\mathcal{D}}$, the values of B_v(mech) $\rightarrow 0$ while the corresponding centrifugal distortion constants approach $+\infty$ (for D_v) or $-\infty$ (for the others) (16, 17). Thus, the differences $[B_v(\text{eff}) - B_v(\text{mech})]$ can be significant for levels lying sufficiently close to dissociation. However, for levels $v = 75$–82 of B-state I_2, these corrections are more than an order of magnitude smaller than the differences seen in column 4 of Table I, so this diagonal rotational coupling cannot be the source of the observed discrepancies.

As was mentioned above, except for one of the two 1_u states, the matrix elements of $\mathbf{H_R}$ between the B state and all other states with the same dissociation limit are identically zero (9). For the remaining case, integration over the electronic coordinates yields the effective coupling functions

$$H_{\beta\beta'}(R) = B(R)[J(J + 1)\mathcal{J}(\mathcal{J} + 1)]^{1/2} = B(R)[6\mathcal{J}(\mathcal{J} + 1)]^{1/2}. \tag{7}$$

In second-order perturbation theory, this coupling term yields level shifts which are proportional to $[\mathcal{J}(\mathcal{J} + 1)]$; they will therefore manifest themselves as further deviations from the simple mechanical B_v values. Since the 1_u state potential lies above the B-state curve, these level energies will be displaced downwards, so this type of coupling will tend to make B_v(obs) $< B_v$(eff), as is observed.

The second-order perturbation theory expression for this level shift is

$$E_{\beta v}^{(2)} = \langle \chi_{\beta v \beta'}^{(1)}(R)|H_{\beta'\beta}(R)|\chi_{\beta v}^{(0)}(R)\rangle \tag{8}$$

where $\chi_{\beta v}^{(0)}(R)$ is the (zeroth-order) radial eigenfunction of the unperturbed B-state level and $\chi_{\beta v \beta'}^{(1)}(R)$ its first-order correction. In the present work the latter was determined by the method of Hutson and Howard (18) as the solution of the linear inhomogeneous differential equation

$$[(-\hbar^2/2\mu)d^2/dR^2 + U_{\beta'}(R) - E_{\beta v}^{(0)}]\chi_{\beta v \beta'}^{(1)}(R) = -H_{\beta'\beta}(R)\chi_{\beta v}^{(0)}(R) \tag{9}$$

where $E_{\beta v}^{(0)}$ is the zeroth-order (unperturbed) energy and $U_{\beta'}(R)$ is the 1_u state potential energy curve. This method is computationally much less expensive and often much more accurate than the traditional approach of expanding $\chi_{\beta v \beta'}^{(1)}(R)$ in terms of the eigenfunctions of the perturbing potential $U_{\beta'}(R)$.

B. Assumed Potential Energy Curves

Determination of the wave functions appearing in Eq. (8) requires knowledge of the potential energy curves for both the $B(0_u^+)$ state and the 1_u state to which it is coupled. The B-state potential is accurately determined by experiment (1, 6, 7). In the present work it was defined by interpolating over RKR turning points and adding a Morse extrapolation at short range. The RKR turning points were generated from near-dissociation expansions for the vibrational energies and B_v values (4, 8, 19), so they should be reliable even at long range.

For the 1_u state, the only information available is Mulliken's (13) prediction that at the ground-state equilibrium distance 2.666 Å its potential curve passes through a point ca. 25 600 cm^{-1} above its dissociation limit. It is therefore a repulsive curve with at most a weakly attractive Van der Waals well at long range. In the present work this potential was assumed to have the form

$$U_{\beta'}(R) = A \exp[-b(R - R_0)] - D(R^*; R)[C_5/R^5 + C_6/R^6 + C_8/R^8] \tag{10}$$

where the function

$$D(R^*; R) = \exp[-4(R^*/R - 1)^3] \qquad \text{for} \qquad R < R^*$$

$$= 1 \qquad \text{for} \qquad R \geqslant R^* \qquad (11)$$

damps the inverse power terms and assures that the potential at small R is largely determined by the exponential term. The constants $A = 25\,600$ cm^{-1}, $b = 2.014$ Å^{-1}, and $R_0 = 2.666$ Å were chosen so that the curve would approximately agree with Mulliken's ([13]) point at $R_0 = 2.666$ Å, while C_5 is predicted by theory ([20]) to be $(-2/3)$ times the C_5 constant for the *B*-state and C_6 and C_8 should be roughly equal to the corresponding *B*-state constants. Using Danyluk and King's ([1]) values of the constants for the *B* state, this yields 1_u-state C_n constants of -1.85×10^5, 17.8×10^5, and 243×10^5 cm^{-1} Å^n, for $n = 5$, 6, and 8, respectively.

The remaining parameter in this 1_u state potential function is the distance R^* at which the damping function $D(R^*; R)$ is turned on. Figure 2 shows the range of potentials which can be generated by choosing different values for this quantity.

C. Results and Discussion

The effect of off-diagonal Coriolis coupling on the B_v constants for *B*-state levels $v = 75$–82 was calculated in the manner described above using 1_u state potential curves corresponding to R^* values ranging from 5 Å to ∞. The resulting $\Delta B_v(R^*)$ predictions are summarized in columns 6–8 of Table I. These predicted differences are largely independent of R^* and are all much smaller than the observed discrepancies, even when one takes account of the relatively large uncertainties in some of the experimental values.

One feature of the above procedure which could invite criticism is the fact that Cummings' ([9]) value for the electronic part of the matrix element of H_R was obtained assuming that the molecular electronic wave function could be approximated by a
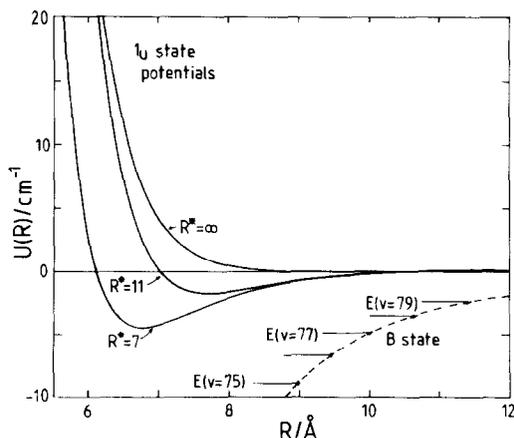
FIG. 2. Behavior of the 1_u state potentials of Eq. (10) (solid curves) for various choices of the damping function parameter R^*. The heavy dashed curve is the *B*-state potential, while the horizontal lines denote the energies of some of its levels.

simple product of atomic wave functions. This basis should certainly be appropriate at large R where interatomic electron overlap is negligible, but at short range it is much less satisfactory. However, the fact that D_v (and other centrifugal distortion constants) approach the limiting behavior predicted for levels near dissociation (4, 16) indicates that the dominant contributions to the second-order energy are associated with large R where this approximation is most appropriate. This affirms the validity of the approximation. As a result, we must conclude that Coriolis (or rotational) coupling *does not* explain the discrepancies $[B_v(\text{mech}) - B_v(\text{obs})]$ listed in Table I.

III. SPIN-ROTATION COUPLING HYPOTHESIS

Spin–rotation coupling is another type of interaction which gives rise to a $\mathscr{J}(\mathscr{J} + 1)$-dependent energy shift, and hence could in principle be responsible for the observed differences. The fine structure term in the Hamiltonian H_{fs} exists because an unpaired electron spin can interact with its environment in the molecule. Part of this operator represents the spin–rotation interaction which arises through coupling between the electron spin magnetic moment and the rotation of the charged nuclei; it may be written as (21)

$$\mathbf{H}_{SR} = -(\hbar e/\mu R^2 c) \sum z_\alpha (\mathscr{J} - \mathbf{J}) \cdot (\mathbf{r}_\alpha \times \mathbf{A}_\alpha) \tag{12}$$

where the magnetic vector potential on nucleus α is

$$A_\alpha = -(ge\hbar/2m_e c) \sum \mathbf{s}_i \times \mathbf{r}_{i\alpha}/r_{i\alpha}^3 \tag{13}$$

and z_α is the nuclear charge, g (=2.00) is the gyromagnetic ratio for the electron, m_e is the electron mass, $\mathbf{r}_\alpha$ is the nuclear position relative to the center of mass, and $\mathbf{r}_{i\alpha} = \mathbf{r}_i - \mathbf{r}_\alpha$ where $\mathbf{r}_i$ is the position of electron i.

In attempting to estimate the effect of this term on the high vibrational levels of B-state I_2, we begin by assuming, as above, that due to the large average internuclear separation the molecular wavefunction can be treated as a product of atomic functions. Since only one valence electron in each atom has unpaired spin, the sum over electrons in Eq. (13) can be truncated to include only one valence electron from each atom. We then make two further approximations:

(i) $r_{11} = r_{22} \simeq \langle r^2 \rangle^{1/2} = 2.53$ Å (9), the expectation value for the radius of an iodine atom valence electron, and
(ii) $r_{12} = r_{21} \simeq R$, and note that $|\mathbf{r}_\alpha| = R/2$.

Replacing each vector cross product by a simple product of magnitudes then yields

$$\mathbf{H}_{SR} = (gz_\alpha \hbar^2 e^2/2\mu c^2 m_e)(1/Rr_{11}^2 + 1/R^3)(\mathscr{J} - \mathbf{J}) \cdot \mathbf{S}$$
$$= \gamma(R)[\mathscr{J} \cdot \mathbf{S} - \mathbf{J} \cdot \mathbf{S}]. \tag{14}$$

The $\mathbf{J} \cdot \mathbf{S}$ term in Eq. (14) does not depend on the (total) rotational quantum number $\mathscr{J}$, so it is dropped from consideration. This leaves a matrix element which is nonzero only for $\Delta\mathscr{J} = 0$ and $\Delta\Omega = 1$. To evaluate it, we assume that the size of the spin

contribution is roughly the same as it would be if *S* were a good quantum number, and that for our $0_u^+ - 1_u$ couplings $S = 1$; this yields

$$\mathbf{H}_{\beta\beta'}^{\mathrm{SR}} = \gamma(R)[S(S + 1)]^{1/2}[\mathscr{J}(\mathscr{J} + 1)]^{1/2} = 2^{1/2}\gamma(R)[\mathscr{J}(\mathscr{J} + 1)]^{1/2}. \qquad (15)$$

The size of the energy shift due to this perturbation operator can readily be calculated using the method described in Section II. However, it is immediately clear that spin–rotation coupling is much too small to account for the B_v discrepancies of Table I, since the coupling function implied by Eqs. (14) and (15) (with energies in cm^{-1} and lengths in Å),

$$\gamma(R) = 10^{-4}(1/R + 6.4/R^3]$$

is much weaker than the Coriolis coupling function $B(R) \simeq 0.3/R^2$ on the whole of the classically accessible interval for the states in question. Moreover, the approximations invoked here were designed to yield an upper-bound estimate of the magnitude of this term. We therefore conclude that spin–rotation coupling makes an even smaller contribution to B_v(obs) than does the Coriolis coupling, and hence conclude that it also cannot be responsible for the observed discrepancies.

IV. SOLUTION OF THE PUZZLE

The two preceding sections report our estimates of the effects of the $\mathscr{J}$-dependent terms in the molecular Hamiltonian which can cause the observed values of B_v to deviate from their predicted mechanical behavior. These coupling terms were shown to be more than an order of magnitude too weak to explain the observed deviations. In the absence of any other plausible explanation, we therefore conclude that the Danyluk–King experiment did not yield the correct experimental B_v values for the vibrational levels in question. In the following, we quote some new data confirming this conclusion and examine the nature of Danyluk and King's (*1*) two-photon sequential absorption spectroscopy experiment to attempt to identify the source of the error.

In a recent laser induced fluorescence study of *B*-state I$_2$ near dissociation, Gerstenkorn and Luc (*10*) obtained improved estimates of the vibrational and rotational constants of the three lowest of the levels studied by Danyluk and King, $v = 78, 79$, and 80. In Table II these new B_v values are compared with both the mechanical behavior predictions of Table I and the experimental values of Danyluk and King (*1*). The Gerstenkorn–Luc constants clearly contradict the latter, and are in excellent agreement with the former. This agreement attests to the predictive ability of the near-dissociation expansion extrapolation and strengthens the above conclusion that the Danyluk–King results are in error.

Two-photon sequential absorption spectroscopy (*1, 22*) is a technique which has the effect of greatly increasing the selectivity achievable in a given experiment. The method requires the use of two lasers, a narrow bandwidth "pump" laser to initially excite the molecules and a relatively broadband "probe" laser to further excite them into an electronic state which will fluoresce to advertise the occurrence of the absorption. In the I$_2$ experiment, the first (pump) laser, whose width was 0.07 cm^{-1}, pumped the molecules from rotational states of the $v_X = 0$ vibrational level of the ground ($X^1\Sigma_g^+$) electronic state into various high vibrational levels of the *B* state. The

TABLE II

Comparison of the Present Near-Dissociation Expansion Extrapolated "Mechanical" Values of B_v with the Experimental Values of Refs. (1) and (10) (Uncertainties in the Last Digits Shown Are Given in Parentheses)

Source	$B_v/10^{-3}$ cm^{-1}		
	v=78	v=79	v=80
Near-dissociation expansion	3.731	3.270	2.813
Gerstenkorn-Luc (1982)	3.738(10)	3.291(10)	2.837(50)
Danyluk-King (1977)	3.577(49)	2.964(69)	2.591(68)

probe laser, of width 1.5 cm^{-1}, then excited these B-state molecules to appropriate rotational components of a single vibrational level of the E state; the subsequent spontaneous $E \rightarrow B$ fluorescence then signals the successful completion of the two photon absorption sequence. A signal will be detected only if the lasers are set so that two successive transitions involving a common B-state level occur at frequences within the respective bandwidths.

The above approach is a very clever procedure, since even for a very congested one-photon spectrum, rotational selection rules will tend to disperse the frequencies of the subsequent transitions allowed for the various B-state levels accessed by a given pump frequency. In the present case, the selection rule $\Delta \mathcal{J} = \pm 1$ defines all of the allowed two-photon transitions originating in $v_X = 0$, passing through high v' levels of the B state, and terminating in the E state. Moreover, the rotational constants of the appropriate vibrational levels of the X and E states are known (1), while the near-dissociation expansions provide good estimates of the vibrational and rotational constants of the high v' levels of the B state. These known (and extrapolated) constants may be used to predict the combinations of pump and probe frequencies, ν(pump) and ν(probe), respectively, which can give rise to successful sequential two-photon absorption. Figure 3 plots such predictions (points) for all allowed transitions originating in $v_X = 0$, $\mathcal{J} = 0$–15, and passing through B-state vibrational levels $v' = 79$–82. Also shown to scale in Fig. 3 is the size of the 1.5×0.07-cm^{-1} selectivity window associated with the lasers used in the Danyluk and King experiment (1).

In Fig. 3, the dispersion along the ν(probe) direction of the points associated with a single value of ν(pump) illustrates the power of this technique for distinguishing among transitions which *could not* be resolved by that same pump laser in a single-photon ($X \rightarrow B$) experiment. Indeed, even though the selectivity window shown appears to be too large to allow transitions involving $v' \gtrsim 79$ to be identified uniquely in the two-photon experiment, the sharpness of the individual lines and regularity of the progressions, coupled with the fact that the same B-state levels were observed using fluorescence from different upper states, provide convincing evidence of the correctness of the original assignments (1). The most likely source of error in the Danyluk–King measurements therefore appears to be method of frequency calibration used in those early two-photon experiments. It involved the use of fairly long
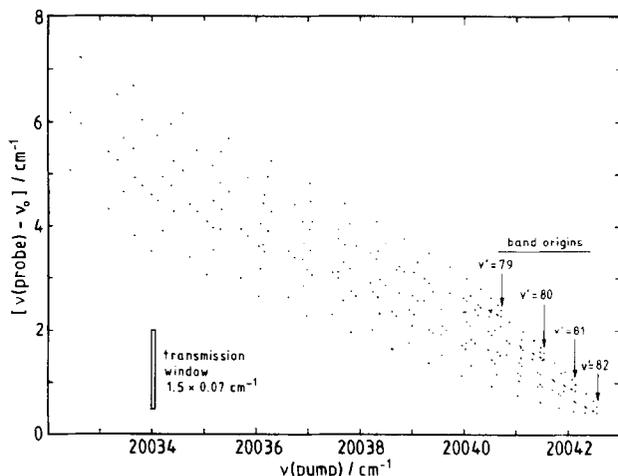
FIG. 3. Plot of all allowed two-photon transitions which originate in $v_x = 0$, $J = 0$–15 and pass through *B*-state levels $v' = 79$–82. An experimentally detected signal has contributions from all points lying within the appropriately placed "transmission window"; ν_0 is an arbitrarily chosen reference frequency.

extrapolations to determine the frequencies of the new lines relative to those of transitions observed and assigned by Barrow and Yee (6).

In any case, it is now clear that the rotational constants of Ref. (1) for *B*-state levels $v' \geq 79$ are in error. A simple illustration of this is provided by the laser-induced fluorescence traces seen in Fig. 4. According to the vibrational and rotational constants of Danyluk and King (1), the $(v, J) = (0, 18) \rightarrow (v', J') = (79, 17)$ line in the
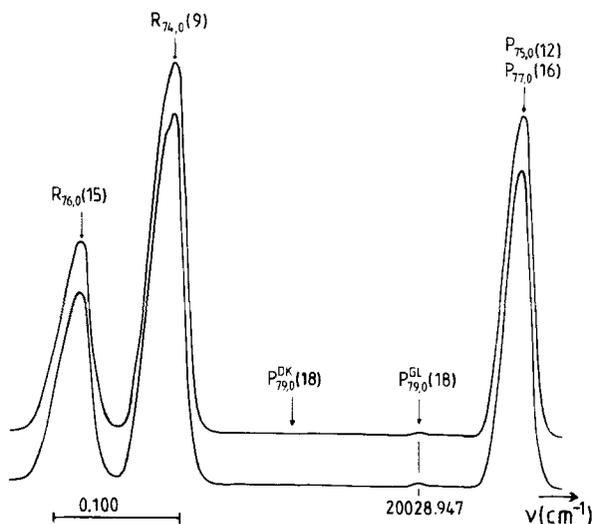
FIG. 4. The agreement between the two independent traces of the one-photon laser induced fluorescence spectrum attests to their reliability. The feature denoted $P_{79,0}^{GL}(18)$ is identified by the Gerstenkorn–Luc (10) constants as the $(0, 18) \rightarrow (79, 17)$ $X \rightarrow B$ transition, while the arrow labelled $P_{79,0}^{DK}(18)$ indicates where the Danyluk–King (1) constants would locate this feature.

$B \rightarrow X$ spectrum should occur at the frequency labeled $P^{DK}_{79,0}(18)$, where the experimental traces are perfectly flat. In contrast, the position of the small peak labeled $P^{GL}_{79,0}(18)$ is accurately predicted by the constants of Gerstenkorn and Luc (*10*).

V. IMPROVED NEAR-DISSOCIATION THEORY CONSTANTS FOR $B(^3\Pi^+_{0u})$ STATE I$_2$

Since the Danyluk and King (*1*) results for $v' \geq 79$ have now been shown to be unreliable, their values of the limiting near-dissociation theory constants for this system should be replaced. Near-dissociation theory shows that for a molecular state whose interaction potential asymptotically dies off as

$$V(R) \simeq \mathcal{D} - C_n/R^n \qquad (16)$$

the pattern of vibrational energies for levels lying sufficiently close to the dissociation limit $\mathcal{D}$ is

$$G(v) = \mathcal{D} - X_0(n)[v_\mathcal{D} - v]^{2n/(n-2)} \qquad (17)$$

where $v_\mathcal{D}$ is the effective (noninteger) vibrational index at dissociation and $X_0(n) = \bar{X}_0(n)/[\mu^n(C_n)^2]^{1/(n-2)}$, where μ is the reduced mass and $\bar{X}_0(n)$ a (known) constant defined by the value of n (*5, 3, 17*). For B-state I$_2$, both theory (*5, 12, 20*) and experiment (*6*) agree that the power $n = 5$, so that $X_0(5) = 9170.912/[\mu^5(C_5)^2]^{1/3}$.

A nonlinear least-squares fit of the $n = 5$ version of Eq. (16) to the Gerstenkorn-Luc (*10*) energies for levels $v = 73$–80 yields the present best estimates of the parameters $\mathcal{D}$, $v_\mathcal{D}$, and C_5 for this state. These constants are believed to be reasonably well converged, since repeating the fits while successively omitting the lowest levels increased the uncertainties but did not significantly affect their values. The results obtained are listed in (the last row of) Table III, where they are compared with previously reported results for this system. The distinctly lower accuracy of the oldest of these sets of results (*24*) is not surprising in view of the fact that they were based on very early (1931!) bandhead measurements (*25*) which were not supplanted until 1972 (*6*). It is interesting to note, however, that within the mutual uncertainties, these first parameter values still agree with the present best estimates. Since they are based on the same data, the small differences between the present recommended parameter values and those of Gerstenkorn and Luc (*10*) arise from the fact that, following

TABLE III

Values of the Near-Dissociation Theory Parameters for B-State ^{127,127}I$_2$ (The Dissociation Energy $\mathcal{D}$ Is Expressed Relative to the Zero Point Level of the Ground $X(^1\Sigma^+_g)$ State)

Source ; year	v' Range	$\mathcal{D}/cm^{-1}$	$v_\mathcal{D}$	$C_5/10^5$ cm^{-1} Å^5
Ref. (24) ; 1971	55-72	20 044.0(±1.2)	87.7(±0.4)	3.11(+0.2)
Ref. (6) ; 1972	64-77	20 043.208(±0.033)	87.345(±0.007)	2.886(±0.006)
Ref. (1) ; 1977	72-82	20 043.063(±0.020)	87.183(±0.012)	2.776(±0.018)
Ref. (10) ; 1982	73-80	20 043.176(±0.008)	87.364(±0.006)	2.850(±0.010)
Recommended; 1983	73-80	20 043.159(±0.019)	87.324(±0.035)	2.884(±0.031)

Barrow and Yee (*6*), they obtained their constants from fits to approximate linearized versions of Eq. (17). This also explains why the parameter uncertainties reported by those two sets of authors are unrealistically small.

VI. CONCLUSIONS

The discrepancies between the experimental results of Danyluk and King (*1*) and the predicted mechanical behavior implied by near-dissociation theory (*3*) have been investigated. Both centrifugal distortion effects and rotational (or Coriolis) and spin–rotation coupling to a nearly repulsive 1_u state have been shown to be much too weak to explain these discrepancies, and they are now attributed to callibration errors in the original experiment. This conclusion is confirmed by more recent experimental results (*10*).

A reanalysis of the Gerstenkorn–Luc (*10*) data for *B*-state levels $v = 73–80$ has yielded new improved estimates of the dissociation energy $\mathcal{D} = 20043.16$ (± 0.02) cm^{-1} of the effective vibrational index at dissociation $v_{\mathcal{D}} = 87.32$ (± 0.04), and of the long-range potential constant $C_5 = 2.88$ (± 0.03) $\times 10^5$ cm^{-1} Å^5. This in turn yields an improved ground-state dissociation energy of $\mathcal{D}_0 = 12440.18$ (± 0.02) cm^{-1}. Although very similar to values of these constants reported previously, the differences are virtually always larger than the uncertainties reported for the earlier values, and the uncertainties given here are believed to be much more realistic. Although these improvements seem small, the fact that this state is almost a touchstone for near-dissociation theory (*3, 5*) and for the development of new experimental spectroscopic techniques makes it important that its properties be understood as thoroughly as possible. Note too that the small changes from the C_5 and $v_{\mathcal{D}}$ constants of Danyluk and King (*1*), which mean that the numerical factors in Eqs. (1) and (2) are ca. 2.6% too large, has no significant effect on the analysis of Sections I–IV.

One interesting result of the present work is its illustration of the utility of near-dissociation theory and near-dissociation expansions for providing a best a priori estimate of "mechanical behavior," deviation from which may signal either experimental error (as in the present case) or the presence of perturbations or changes in the nature of the intermolecular forces. It also provides another convincing example of the utility of Hutson's (*18*) procedure for performing perturbation theory calculations.

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