

## Improved spectroscopic constants for $I_2$ D $1\Sigma_u^+$

Melvin L. Nowlin<sup>1</sup>, Michael C. Heaven<sup>\*</sup>

*Department of Chemistry, Emory University, Atlanta, GA 30322, USA*

Received 9 March 1995

### Abstract

The D–X transition of  $I_2$  can be used to observe populations in vibrationally excited levels of  $I_2(X)$ . Levels in the range  $20 \leq v'' \leq 50$  are sensitively detected by exciting transitions that terminate on  $I_2(D)$   $v' \leq 40$ . In the present work, spectroscopic studies of the lower vibrational levels of  $I_2(D)$  were performed to facilitate use of the D–X transition for monitoring excited  $I_2(X)$ . New molecular constants for the D state are reported.

### 1. Introduction

The  $D(0_u^+) - X(0_g^+)$  transition of  $I_2$  has been studied for more than eighty years. In the vacuum ultraviolet region the strong  $D \leftarrow X$  absorption bands are commonly known as the Cordes system [1–4].  $D \rightarrow X$  emission is readily observed when the D state is excited by VUV light or discharges [5–9]. The long-wavelength segment of the emission spectrum corresponds to a bound–free transition. The features of this highly structured continuum spectrum are known as the McLennan bands [5].

Our interest in the  $I_2$  D–X system derives from its potential use for monitoring highly excited vibrational levels of  $I_2(X)$  (denoted as  $I_2^{\dagger}$  in the following). Due to large differences between the X and D state equilibrium internuclear distances, transitions suitable for observing  $I_2^{\dagger}$  ( $v'' > 20$ ) terminate on the

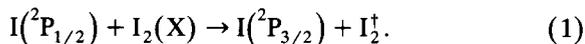
$0 \leq v' \leq 40$  vibrational levels of  $I_2(D)$ . These transitions fall in the near-UV spectral range (250–300 nm), so they may be excited by conventional tunable laser systems. As the D state has a short radiative lifetime ( $\approx 10$  ns) and a high fluorescence quantum yield, the D–X transition is well suited for laser-induced fluorescence (LIF) detection of  $I_2^{\dagger}$ . Furthermore, owing to the occurrence of a maximum in the Mulliken difference potential, the most intense bound–free emission appears at 321 nm, regardless of the D state level from which the transition originates [10]. Consequently, a band-pass filter can be used to isolate the D–X fluorescence without introducing a dependence of the detection sensitivity on the D state vibrational levels used in LIF probing. This feature is attractive for applications where  $I_2^{\dagger}$  is to be monitored in a bright chemiluminescent environment (see, for example, Ref. [11]). In particular, D–X probing is ideal for characterizing  $I_2^{\dagger}$  in chemical oxygen iodine laser (COIL) systems.

In recent experiments, we have used the D–X transition to observe collisional ro-vibrational energy transfer between excited levels of  $I_2(X)$  [12,13], and

<sup>\*</sup> Corresponding author.

<sup>1</sup> Present address: HQ USAFA/DFC, United States Air Force Academy, CO 80840, USA.

to map the nascent ro-vibrational population distribution resulting from the electronic to vibrational energy transfer process [14]



To analyze the spectra obtained in these measurements, we used the best available spectroscopic constants to predict the line positions [15,16]. For the lower D state vibrational levels the most accurate data has been obtained by Ishiwata and Tanaka [15], who used optical–optical double resonance techniques. However, predictions of the energies of D,  $v' < 10$  levels, based on Ishiwata and Tanaka's [15] constants, were in error by more than  $1 \text{ cm}^{-1}$ . Although this error is relatively small, we found that a predictive accuracy of  $\pm 0.08 \text{ cm}^{-1}$  was needed for assignment and line intensity analysis of the congested spectra obtained by probing the products of reaction (1). Therefore, we have used data taken in the course of energy transfer measurements to determine spectroscopic constants that are valid for the lower vibrational levels ( $v' < 40$ ) of  $I_2(D)$ . In addition, we have combined our data with results from previous laser excitation studies [3,4,15] to define a set of vibrational constants that are accurate for the range  $0 \leq v' \leq 290$ .

## 2. Experimental

The apparatus used for these experiments has been described previously [13]. Excited vibrational levels of  $I_2(X)$  were populated by stimulated emission pumping (SEP) via the  $B(0_u^+) - X(0_g^+)$  transition. The D–X bands originating from the prepared levels were then observed by LIF. Two slightly different schemes were used for the SEP step. In the first set of measurements, an Nd/YAG pumped dye laser was used to generate the pump and dump pulses. The pump laser ( $0.05 \text{ cm}^{-1}$  linewidth) was tuned to the B–X, 7–2 R(47) line ( $16117.15 \text{ cm}^{-1}$ ). This transition was chosen as the 1064 nm fundamental from the Nd/YAG laser could then be used to stimulate down on the 7–38 P(49) line ( $9393.64 \text{ cm}^{-1}$ ). An optical delay was used to separate the pump and dump pulses by approximately 10 ns. A frequency doubled dye laser (probe), operated with an intra-

cavity étalon, was used to observe ro-vibrationally excited  $I_2(X)$ . LIF from the D–X transition was dispersed by a 0.25 m monochromator and detected by a photomultiplier. The monochromator was set to transmit a 6 nm wide band, centered at 321 nm. Absolute wavenumber calibration of the probe laser was achieved by directing a portion of the fundamental through an  $I_2$  cell, and recording the B–X spectrum. The wavenumbers for the B–X lines were taken from the atlas of Gerstenkorn and Luc [17].

In the second set of measurements, independent pulsed dye lasers were used to supply the pump and dump pulses. The pump laser was set to excite the B–X, 19–1 R(55) line ( $17767.97 \text{ cm}^{-1}$ ). The dump laser then stimulated down on the 19–23, P(57) line ( $13189.76 \text{ cm}^{-1}$ ).

Population of a single ro-vibrational level by SEP is ideal for energy transfer measurements, but observations of a range of rotational levels are needed to define accurate spectroscopic constants. Hence,  $I_2$  was mixed with an inert collision gas (usually He or Ar) to promote rotational relaxation. For gas mixtures consisting of 30 mTorr of  $I_2$  in 500 mTorr of the collision partner, delays of 100–200 ns between the dump and probe pulses were sufficient to permit adequate rotational relaxation.

## 3. Results and analysis

Fig. 1 shows a typical example of the D–X spectra obtained in these measurements. Note that transitions originating from even rotational levels are missing in this spectrum, due to the  $\Delta J = \text{even}$  selection rule that governs collisional energy transfer for a homonuclear diatomic molecule. Probing of the D state vibrational manifold was restricted by the Franck–Condon factors. Excitation from X,  $v'' = 23$  gave access to the levels D,  $30 \leq v' \leq 37$ . Similarly, the levels D,  $4 \leq v' \leq 11$  were excited from X,  $v'' = 38$ .

As the SEP state preparation method was uniquely selective, rotationally resolved D–X spectra were easily assigned. Even after partial collisional relaxation, lines originating from the initially populated levels were more intense than all other features. For each vibrational band, the band origin and rotational

constants were obtained by fitting the line positions to the expression

$$\nu = \nu_{v',v''} + B'_v J'(J' + 1) - D'_v [J'(J' + 1)]^2 - B''_v J''(J'' + 1) + D''_v [J''(J'' + 1)]^2. \quad (2)$$

Trial fits where the distortion constants were treated as variables did not yield statistically significant values for these parameters. In the next round of fitting, the distortion constants for the lower levels were fixed at the values given by Bacis et al. [16] ( $D''_{23} = 5.449 \times 10^{-9}$ ,  $D''_{38} = 6.766 \times 10^{-9}$  cm $^{-1}$ ). Even with this constraint, the  $D'_v$  values obtained were of marginal significance. Consequently, the D state distortion constants were fixed at calculated values (see below) in the final fits.

Lower state rotational constants were found to be in excellent agreement with those obtained by Bacis et al. [16] and Tellinghuisen et al. [8]. As these earlier studies of the ground state were of greater accuracy than our measurements, the final fits to Eq. (2) were made with the lower rotational constants fixed at the values given by Bacis et al. [16]. This scheme yielded D state rotational constants that were in agreement with the values reported by Ishiwata and Tanaka [15]. Vibrational term energies for the D state were calculated by adding the ground state

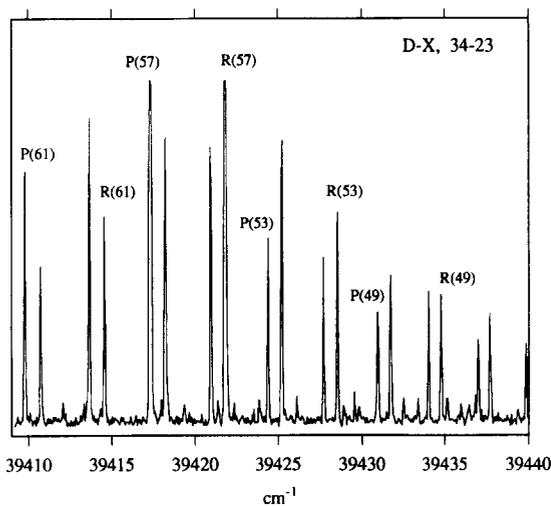


Fig. 1. Laser excitation spectrum for the D–X system. This trace was recorded following SEP preparation of  $v'' = 23$ ,  $J'' = 57$ . Collisions with Ar were used to broaden the range of rotational levels populated.

Table 1

Term energies and spectroscopic constants for I $_2$ (D)

$v'$	$\nu$ (cm $^{-1}$ ) <sup>a</sup>	$B^b$ (10 $^{-2}$ cm $^{-1}$ )	$D^c$ (10 $^{-9}$ cm $^{-1}$ )
4	41451.97(6)	2.0516	3.90
5	41545.84(4)	2.0472	3.89
6	41639.56(5)	2.0227	3.89
7	41733.01(7)	2.0382	3.88
8	41826.28(5)	2.0337	3.88
9	41919.19(6)	2.0292	3.87
10	42011.95(7)	2.0246	3.87
11	42104.47(4)	2.0201	3.87
30	43810.37(7)	1.9316	3.87
31	43897.37(6)	1.9268	3.88
32	43984.05(4)	1.9221	3.88
33	44070.47(4)	1.9173	3.88
34	44156.55(5)	1.9126	3.88
35	44242.35(5)	1.9078	3.89
36	44327.85(6)	1.9030	3.89
37	44413.09(6)	1.8983	3.89

<sup>a</sup> Numbers in parentheses are 1 $\sigma$  errors for the least significant figure.

<sup>b</sup> Rotational constants from Ref. [15].

<sup>c</sup> Calculated centrifugal distortion constants.

vibrational energies [16] to the fitted band origins. The resulting vibronic term energies (relative to the ground state minimum) are listed in Table 1.

The new term energies were compared with energies predicted using the constants of Ishiwata and Tanaka [15]. At  $v'' = 34$  the predicted energies were in error by 0.36 cm $^{-1}$ . This error increased with decreasing  $v''$ , reaching a value of 1.77 cm $^{-1}$  at  $v' = 5$ . Comparisons with energies predicted from the constants of Bartels et al. [3], and Hoy and Lipson [4] revealed essentially the same discrepancies.

An improved D state electronic term energy ( $T_e$ ) and low-order vibrational constants were obtained by fitting the Dunham expansion

$$T^D(v) = \sum_n Y_{n,0} (v + \frac{1}{2})^n \quad (3)$$

to the data from Table 1. The following constants were obtained (all in cm $^{-1}$ ):

$$Y_{00}(T_e) = 41026.10(7), \quad Y_{10}(\omega_e) = 95.157(15),$$

$$Y_{20}(-\omega_e x_e) = -0.1174(8),$$

$$Y_{30}(w_e y_e) = -3.1(1) \times 10^{-4},$$

where the numbers in parentheses are the  $1\sigma$  errors for the least significant figures. The standard deviation for this fit was  $0.04 \text{ cm}^{-1}$ . Tellinghuisen [7] derived term energies for the lowest vibrational levels of the D state ( $0 \leq v' \leq 3$ ) from vibrationally resolved emission spectra. Extrapolation using the above constants yielded term energies that differed from Tellinghuisen's results by (observed – calculated)  $1.3$  ( $v' = 0$ ),  $0.9$  ( $v' = 1$ ),  $1.0$  ( $v' = 2$ ), and  $0.3 \text{ cm}^{-1}$  ( $v' = 3$ ). This is a satisfactory level of agreement, given the estimated precision of  $1\text{--}2 \text{ cm}^{-1}$  for the experimental data [7].

To obtain improved spectroscopic constants for  $I_2(\text{D})$  over the range  $0 \leq v \leq 290$ , we combined our results with existing data for the levels above  $v' = 37$ . Ishiwata and Tanaka [15] reported constants that were obtained by simultaneous fitting of the rotational and vibrational constants (see below). For use in the merging exercise presented here, Ishiwata [18] provided a list of band origins for the range  $0 \leq v' \leq 124$ . These were derived from the original (unpublished) data [15]. As these origins were most reliable for  $v' \geq 74$ , we merged our data for  $v' \leq 37$  with Ishiwata's results for  $74 \leq v' \leq 124$ . Vibronic term energies for the ranges  $125 \leq v' \leq 201$  and  $202 \leq v' \leq 290$  were taken from the studies of Bartels et al. [3] and Hoy and Lipson [4], respectively. The complete set of vibronic term energies was used in a weighted fit to Eq. (3). For  $74 \leq v' \leq 124$  the origins were weighted according to the inverse squares of their standard deviations (ranging from  $0.01$  to  $0.13 \text{ cm}^{-1}$ , with typical values around  $0.04 \text{ cm}^{-1}$ ). Bar-

tels et al. [3] estimated that their measurements were accurate to within  $0.5 \text{ cm}^{-1}$ , and this value was used as the standard deviation for all levels above  $v' = 124$ . Hoy and Lipson [4] estimated that their band edges were accurate to within  $0.3 \text{ cm}^{-1}$ , but we used the slightly more pessimistic value to prevent the fit from being dominated by the preponderance of high  $v'$  data. A satisfactory fit was achieved using a ninth-order polynomial (systematic oscillations were evident in the residuals of all lower-order fits). As the constants obtained were highly correlated, they were subjected to a rounding procedure that preserves their accuracy [19]. The final constants are given in Table 2, where they are compared with several previous estimates. The residuals of the fit, determined for the rounded constants, are plotted in Fig. 2.

As noted above, the D state distortion constants could not be obtained by direct fitting. Instead, they were calculated from the RKR potential energy curve defined by the revised constants. The calculated distortion constants (listed in Table 1) were used in an iterative process to refine the fits to Eq. (2). Only one cycle of this procedure was needed, as the first-pass corrections to the band origins and rotational constants were less than their  $1\sigma$  standard deviations.

In the studies of Bartels et al. [3] and Hoy and Lipson [4], data for high vibrational levels of  $I_2(\text{D})$  were combined with band origins determined from the constants of Ishiwata and Tanaka [15]. Hence, the agreement between the low-order constants seen

Table 2  
Electronic term energies and vibrational constants for  $I_2(\text{D})$  ( $\text{cm}^{-1}$ )

Constant	Present work	Ref. [9]	Ref. [15]	Ref. [3]	Ref. [4]
$Y_{00}(T_e)$	41026.47(7)	41026.4(4)	41028.584(47)	41028.584(47)	41028.542(72)
$Y_{10}(\omega_e)$	95.0452(126)	95.66(21)	94.9928(60)	95.0108(286)	94.99697(1149)
$Y_{20}(-\omega_e x_e)$	-0.10536(78)	-0.1345(50)	-0.10919(26)	-0.11008(155)	-0.108789(590)
$Y_{30}/10^{-4}$	-8.104(227)	-2.14(43)	-5.805(50)	-5.759(310)	-6.1458(1378)
$Y_{40}/10^{-6}$	8.588(374)	1.3(2)	3.686(43)	3.936(287)	4.4999(1706)
$Y_{50}/10^{-9}$	-60.11(369)	-1.7(2)	-7.61(13) <sup>b</sup>	-11.22(124)	-15.718(1194)
$Y_{60}/10^{-11}$	30.65(221)	-	-	1.367(204)	3.289(474)
$Y_{70}/10^{-13}$	-10.0(8)	-	-	-	-0.364(10)
$Y_{80}/10^{-16}$	18.2(15)	-	-	-	0.130(86)
$Y_{90}/10^{-18}$	-1.4(1)	-	-	-	-

<sup>a</sup> The  $1\sigma$  uncertainties for these constants are given in parentheses

<sup>b</sup> Due to a typographical error this is given as a positive constant in Ref. [15].

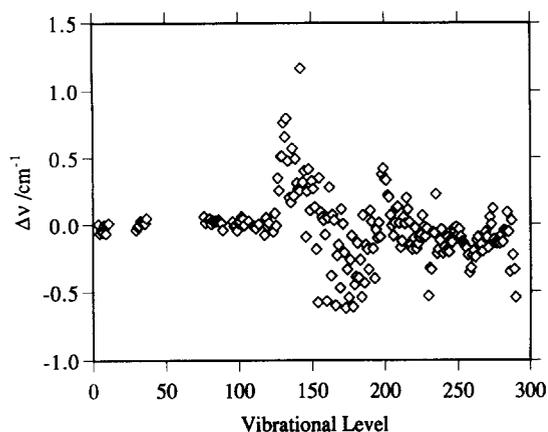


Fig. 2. Residuals (observed–calculated term energies) for a ninth-order fit to  $I_2(D)$  levels in the range  $4 \leq v' \leq 290$ .

in the last three rows of Table 2 is to be expected. It is the discrepancy between the present results and those of Ishiwata and Tanaka [15] that requires comment. Ishiwata [18] noted that the  $v' < 74$  levels were observed via two-photon B–D transitions in the 680–850 nm range. Absolute wavenumber calibration was established against the relatively sparse opto-galvanic spectrum of Ne. Uncertainties in the absolute calibration are the most probably cause of the discrepancy. Fortunately, it appears that the relative wavenumber scale was reliable. This is supported by the fact that our rotational constants were in good agreement with those predicted by Ishiwata and Tanaka's [15] rotational polynomial.

#### 4. Summary

Laser-induced fluorescence techniques were used to characterize vibrational levels of  $I_2(D)$  in the range  $4 \leq v' \leq 37$ . These results were combined with data from earlier studies to define an improved electronic term energy, and vibrational constants valid for the range  $0 \leq v' \leq 290$ . To facilitate future analyses of D–X line intensity data, a new RKR curve, and a matrix of D–X Franck–Condon factors have

been calculated. These are available from the authors on request.

#### Acknowledgement

We thank Professor Takishi Ishiwata for calculating band origins from his data, and making these results available to us. We also thank Professor Joel Tellinghuisen for several helpful discussions, and the programs used to calculate RKR curves, distortion constants, and Franck–Condon factors. This work was supported by the Air Force Office of Scientific Research under grant F49620-95-1-0010.

#### References

- [1] H. Cordes, *Z. Physik* 97 (1935) 603.
- [2] A. Hiraya, K. Shobatake, R.J. Donovan and A. Hopkirk, *J. Chem. Phys.* 88 (1988) 52.
- [3] M. Bartels, R.J. Donovan, A.J. Holmes, P.P.R. Langridge-Smith, M.A. MacDonald and T. Ridley, *J. Chem. Phys.* 91 (1989) 7355.
- [4] A.R. Hoy and R.H. Lipson, *Chem. Phys.* 140 (1990) 187.
- [5] J.C. McLennan, *Proc. Roy. Soc. A* 88 (1913) 289.
- [6] J. Tellinghuisen, *Chem. Phys. Letters* 29 (1974) 359
- [7] J. Tellinghuisen, *Chem. Phys. Letters* 99 (1983) 373
- [8] J. Tellinghuisen, M.R. McKeever and A. Sur, *J. Mol. Spectry.* 82 (1980) 225.
- [9] J. Tellinghuisen, *Can. J. Phys.* 62 (1984) 1933.
- [10] J. Tellinghuisen, *Advan. Chem. Phys.* 60 (1985) 299.
- [11] P. Crozet, R. Bacis, A. Bouvier, A.J. Bouvier, S. Churassy and J.P. Pique, *J. Phys. (Paris) C* 48 (1987) 385.
- [12] M.L. Nowlin and M.C. Heaven, *J. Chem. Phys.* 99 (1993) 5654.
- [13] M.L. Nowlin and M.C. Heaven, *J. Phys. IV (Paris)* C4 (1994) 729.
- [14] M.L. Nowlin, Ph.D. Thesis, Emory University (1994).
- [15] T. Ishiwata and I. Tanaka, *Laser Chem.* 7 (1987) 79.
- [16] R. Bacis, D. Cerny and F. Martin, *J. Mol. Spectry.* 116 (1986) 71.
- [17] S. Gerstenkorn and P. Luc, *Atlas du spectre d'absorption de la molécule d'iode*, Laboratoire Aime Cotton, CNRS II, Orsay, France (1977).
- [18] T. Ishiwata, private communication.
- [19] J. Tellinghuisen, *J. Mol. Spectry.* 137 (1989) 248.