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# Laser excitation and photoionization spectroscopy of the $AO^+$ and B1 states of indium monoiodide: Ground state dissociation energy and photodissociation yield of $\ln(6s^2S_{1/2})$

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The dissociation energy of the InI ground state  $(X^{1}\Sigma^{+}(O^{+}))$  and the relative yield of  $In(6s^{2}S_{1/2})$  from the photodissociation of InI by sequential two-photon absorption have been measured by laser-induced fluorescence and excitation spectroscopy in the 390–431 nm region. Laser excitation spectroscopy and photoionization experiments demonstrate that the  $XO^{+}$  dissociation energy is  $25 340 \pm 90 \text{ cm}^{-1}$ , which agrees with the value suggested by Vempati and Jones [J. Mol. Spectrosc. **127**, 232 (1988)] if the InI ground state is covalent. Seven previously unreported vibrational bands of the InI( $B \leftarrow X$ ) transition have been observed and the molecular emission spectra indicate that the  $B^{3}\Pi_{1}(1)$  state is predissociated above v = 6. Splitting between the fine structure levels of the In  $np^{2}P_{1/2,3/2}$  ( $15 \le n \le 17$ ) states has also been measured by fluorescence suppression spectroscopy, following the three photon excitation of InI in the 450–470 nm interval. © 1999 American Institute of Physics. [S0021-9606(99)01827-9]

### I. INTRODUCTION

In 1934, Wehrli and Miescher<sup>1,2</sup> reported the observation of three excited states of InI. The two lowest lying of these are bound and were labeled  $A^{3}\Pi_{0}$  and  $B^{3}\Pi_{1}$ , while transitions from ground to the third state, denoted  $C^{1}\Pi_{1}$ , give rise to a broad continuum in the ultraviolet ( $\lambda \sim 318$  nm). From microwave absorption experiments, Barrett and Mandel<sup>3</sup> subsequently determined the rotational constants for the ground states of the monohalides of aluminum, gallium, and indium. Schenk et al.4 extended the work of Ref. 3 by including hyperfine structure in the analysis of the InI rotational spectrum. With the Kitt Peak Fourier-transform spectrometer, Davis and Pecyner<sup>5</sup> measured the rotational line positions for 234 vibrational bands of the  $A, B \leftarrow X$  transitions in absorption in the 22 285–25 322 cm<sup>-1</sup> region and determined vibrational and rotational spectroscopic constants for the X, A, and B states.

Despite the availability of high-resolution absorption measurements, a significant issue yet to be resolved for InI is the dissociation energy of the ground state  $(X \, {}^{1}\Sigma^{+}(O^{+}))$ .<sup>6</sup> Primarily on the basis of thermochemical data, Barrow<sup>7</sup> suggested that  $D_0(X) \sim 27\,600 \,\mathrm{cm}^{-1}$ , which is 7%–15% larger than the values estimated by Bulewicz *et al.*<sup>8</sup> and Wehrli and Miescher<sup>1</sup> from flame photometry and spectroscopic experiments, respectively. Vempati and Jones<sup>9–11</sup> determined the rotational constants of the *A* and *B* states from an analysis of microwave discharge emission spectra and concluded that the InI(*X*) state dissociation energy is 25 296 cm<sup>-1</sup> if *XO*<sup>+</sup> is covalent and correlates, in the separated atom limit, with

In  $(5p {}^{2}P_{1/2}) + I(5p {}^{2}P_{3/2})$ . Presuming, however, that the ground state is ionic, Vempati and Jones<sup>11</sup> concluded that *the*  $AO^+$  and B1 states are also derived from  $In(5p {}^{2}P_{1/2}) + I({}^{2}P_{3/2})$  and the ground-state dissociation energy rises to  $\sim 27500 \text{ cm}^{-1}$ . The latter scenario was favored in Ref. 11 on the basis of molecular orbital correlation arguments.

Spectroscopic constants for electronic states of InI and other Group IIIA metal-halide diatomics are of interest for several reasons, one of which is the role of these species in gas discharge lamps.<sup>12</sup> Furthermore, measurements of relative photodissociation yields of metal atoms in specific excited states or metal-halogen atomic ion pairs<sup>13</sup> are vital to determining the practicality of thin film deposition<sup>14</sup> or laser<sup>15</sup> schemes. In this paper, the results of laser spectroscopic experimental studies of the A and B states of InI are reported. Laser-induced fluorescence and excitation spectroscopy in the 390-431 nm region reveal seven previously unreported  $B \leftarrow X(v' - v'')$  bands, and the spectra suggest that the B1 state is predissociated above v' = 6. Comparison of  $B, A \leftarrow X$  absorption spectra with the wavelength-dependent relative yield of  $In(6s^2S_{1/2})$  shows that the upper limit on  $D_e$  for the InI(X) state is 25 429 cm<sup>-1</sup>. Photoionization spectra acquired in the vicinity of the I<sup>-</sup> photodetachment threshold reveal that a conservative *lower limit* on  $D_e(X)$  is 25 143  $cm^{-1}$ . These values support the proposal by Barrow<sup>7</sup> that the InI ground state is covalent and derived from  $In({}^{2}P_{1/2})$  $+ I(^{2}P_{3/2}).$ 

The photodissociation spectra also exhibit a strong dependence of  $\ln(6s^2S_{1/2})$  yield on the rotational quantum number of the intermediate [B1(v',J')] state, a characteristic that is not present in the photoionization spectra. Finally, splitting between the fine structure components of the  $np^2P_J$  ( $n \le 17$ ) states of In and the dipole-forbidden  $ns^2S_{1/2}$ ,  $md^2D_{3/2,5/2} \leftarrow 6s^2S_{1/2}$  ( $15 \le n \le 25$ ,  $13 \le m \le 25$ )

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transitions have been observed by fluorescence suppression spectroscopy of the  $In(6s^2S_{1/2})$  species, following three-photon excitation of InI in the 450–470 nm spectral region.

### **II. EXPERIMENTAL APPARATUS AND TECHNIQUES**

All experiments were conducted under static fill conditions with InI-containing quartz optical cells. After the cells were evacuated to below  $10^{-6}$  Torr and outgassed, natural abundance InI was introduced and the cell sealed. For most of the experiments described here, the cells were operated at a temperature of 650±5 K, which corresponds to an InI number density of 10<sup>16</sup> cm<sup>-3</sup>. Radiation from an Nd:YAG laser-pumped dye laser having a linewidth of  $\sim 0.1 \text{ cm}^{-1}$  was directed along the axis of the cell and fluorescence observed at right angles by a 0.25 m monochromator and a photomultiplier. Experiments were conducted in which either atomic In or laser-induced  $InI(B, A \rightarrow X)$  emission was detected. The dye laser wavelength was calibrated by Ne optogalvanic spectroscopy to an estimated uncertainty of  $\pm 0.1$  cm<sup>-1</sup>. The nominal dye laser pulsewidth is 8 ns and the pulse energy was, unless noted otherwise, maintained at  $\sim 1$  mJ. A boxcar integrator sampled the photomultiplier output and the entire experiment was under the control of a computer.

Survey absorption spectra of InI were obtained at a resolution of 0.2 nm with a Xe arc lamp providing the source continuum and a 1 m spectrograph (having a reciprocal dispersion of 0.82 nm/mm in first order) equipped with a diode array. The spectral dependence of the lamp output was accounted for by sampling the beam incident upon and transmitted by the optical cell with fiber bundles and an optical multichannel analyzer.

Photoionization experiments were also conducted in which the optical cell was replaced by a proportional counter which is simply a Pyrex tube, 32 cm in length, having a cylindrical diode. The anode is a 150  $\mu$ m diameter nickel wire suspended along the axis of a cylindrical stainless-steel cathode by Ni–W feedthroughs. The cell windows are Suprasil-grade quartz and, after introducing InI, the counter was backfilled with 150 mTorr of He. A buffer amplifier was inserted into the signal path between the ionization cell and boxcar amplifier. Bias voltages between ~200 and ~350 V were required to operate the diode in the linear portion of its response (signal vs voltage) characteristic.

### **III. RESULTS AND DISCUSSION**

# A. Molecular $(B \leftarrow X)$ and atomic $(\ln(6^2 S_{1/2}))$ excitation spectra

Figure 1 shows the absorption spectrum for InI at 650 K in the 300–425 nm region. The highly structured B1  $\leftarrow XO^+$  and  $AO^+ \leftarrow XO^+$  bands as well as the  $C1 \leftarrow XO^+$ continuum dominate the spectrum. The latter is clearly saturated and the six strongest features in the  $B1 \leftarrow XO^+$  spectrum (lying between 399 and 403 nm) are all members of the  $v' - v'' \equiv \Delta v = 0$  progression. Simulations of the experimental  $A, B \leftarrow X$  absorption spectra, calculated from the spectroscopic constants of Refs. 5 and 11, match the data of Fig. 1 and higher-resolution measurements ( $\Delta\lambda < 0.1$  nm, cf. Fig. 8) quite well.



FIG. 1. Absorption spectrum of InI in the 300–425 nm region. The C1  $\leftarrow XO^+$  continuum is saturated between ~324 and 326 nm and the highly structured bands are associated with  $AO^+$ ,  $B1 \leftarrow X$  transitions of the molecule. For these data, the cell temperature was 650 K, which corresponds to  $[InI] \approx 10^{16} \text{ cm}^{-3}$ .

A series of experiments was conducted in which molecular and atomic excitation spectra were obtained. Molecular spectra were acquired predominantly for the *B*1 state which involved monitoring the relative intensity of a particular  $B \rightarrow X(v',v'')$  emission line as the dye laser wavelength was scanned. This experimental approach is essentially a sensitive means for acquiring  $B \leftarrow X$  absorption spectra. Similarly, atomic excitation spectra for the In 6  ${}^{2}S_{1/2}$  state were obtained by recording the relative intensity of the  $6s {}^{2}S_{1/2} \rightarrow 5p {}^{2}P_{3/2}$  atomic line (451.1 nm) as a function of dye laser wavelength. Results representative of more than 20 spectra acquired in the 390–410 nm interval are illustrated in Figs. 2–5.

The  $\ln(6s^2S_{1/2})$  excitation spectrum in the 390–410 nm interval is illustrated in Fig. 2. Upon examining the data, it is evident that features attributable to the  $AO^+$  state are con-



FIG. 2. Overview of the laser excitation spectrum of  $\ln(6s^2S_{1/2})$  in the violet (390–410 nm). Note the clear, red-degraded vibrational bands of the  $B \leftarrow X$  transition lying between ~390 and 394 nm.  $B \leftarrow X$  vibrational bands associated with other prominent features in the spectrum are also indicated.



FIG. 3. (a) InI molecular fluorescence spectrum obtained over the 391–398 nm interval by monitoring the  $B \leftarrow X(v' - v'') = (1-1)$  transition at 399.9 nm, and (b) the atomic  $\ln(6s^2 S_{1/2})$  excitation spectrum over the same spectral region. Several of the most prominent  $B \leftarrow X$  bands are labeled.

spicuous by their absence. Only intermediate resonances associated with the *B*1 level are observed, and several are labeled in Fig. 2. Notice, however, that well-developed vibrational bands are present only in the short wavelength portion of the spectrum. For  $\lambda \gtrsim 395$  nm, the features are, in general, considerably sharper, and beyond ~400 nm the spectrum rapidly diminishes in intensity.

A detailed comparison of the  $In(6 {}^{2}S_{1/2})$  excitation spectrum with corresponding portions of the B1(v') excitation spectra reveal several trends that are illustrated in Figs. 3–5. Parts (b) and (a) of Fig. 3, for example, show (respectively)



FIG. 4. Spectra similar to those of Fig. 3 over the 401–411 nm region. The molecular laser-induced fluorescence spectrum was acquired by monitoring the  $B(v'=1) \rightarrow X(v''=1)$  transition.



FIG. 5. Comparison of: (a) the molecular excitation spectrum recorded by monitoring  $B(v'=3) \rightarrow X(v''=5)$  fluorescence at 406.8 nm, and (b) the In(6  ${}^{2}S_{1/2})$  excitation spectrum in the 395–403 nm region.

the In( $6s^2S_{1/2}$ ) excitation spectrum in the 391–398 nm region along with the molecular excitation spectrum obtained by monitoring only the  $B \rightarrow X(v' - v'' = 1 - 1)$  transition at 399.9 nm. The strongest feature in the molecular spectrum, the (1-0) band, has a profile consistent with previous absorption and emission experiments.<sup>1,10</sup> Because the rotational constants  $(B_e)$  for the  $XO_e^+$  and B1 states differ by  $<10^{-3}$  cm<sup>-1</sup> (Refs. 10, 11), additional heads often appear in the P, Q, or R branches of vibrational bands at large J. The extra head evident here [Fig. 3(a)] is also present in the (1-1) band. Of particular interest, however, is the structure in the photodissociation (In 6  ${}^{2}S_{1/2}$  yield) spectrum and its correlation with the (1-0) absorption (excitation) profile. Note that maximum  $\ln 6^{2}S_{1/2}$  yield is sharply peaked and does not coincide with maximum absorption. Rather, In excited-state production is clearly enhanced by high J intermediate states of the R (and possibly Q) branch. Similarly, when the B(v'=0) excitation spectrum (not shown) was obtained by monitoring the  $B \rightarrow X(0-2)$  transition at 405.0 nm, peak (0-0) P-branch absorption was observed to coincide with a small suppression in the  $In(6^{2}S)$  yield and, conversely, maximum yield is associated with high J values of the R branch. Almost identical results were obtained for the (1-1) band which was observed by monitoring the (1-0)transition at 397.0 nm. Similar behavior is observed elsewhere as evidenced at longer wavelengths (401-411 nm) by the spectra of Fig. 4. In absorption, the  $B \leftarrow X(1-2)$  and (1-3) bands exhibit the well-known violet-degraded profiles, but additional peaks appear in the In 6  $^{2}S$  yield spectra, demonstrating that photodissociation yield is dependent upon J. Higher v' states were also examined and illustrate these effects most clearly. Figure 5, for example, shows the atomic and molecular excitation spectra for several (3-v'') band heads. As discussed by Vempati and Jones,<sup>10</sup> shading of the  $B \leftarrow X$  bands reverses for  $2 \le v' \le 3$  owing to the rapid variation of  $B_{v'}$  with v'. Consequently, the (3-v'') bands are red degraded but it is again the influence of the rotational quantum number on the atomic excitation spectra that is the most intriguing aspect of these spectra. Consider the lower (atomic

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 $\begin{array}{c} 1 & 1 & 1 & 6s^2S_{1/2} & 5p^2P_{1/2} \\ (1-3) & (3-5) & (2-4) & (1-4) & (2-5) & (2-4) & (1-4) & (2-5) & (2-4) & (1-4) & (2-5) & (2-4) & (2-5) & (2-4) & (2-5) & (2-6) &$ 

FIG. 6.  $\ln(6 {}^{2}S_{1/2})$  excitation spectrum recorded at a dye laser resolution of ~0.1 cm<sup>-1</sup> in the 402–411 nm region. All of the labeled vibrational band features are associated with  $B \leftarrow X$  transitions.

excitation) spectrum of Fig. 5, which shows the presence of three distinct features associated with the (3-v'') bands shown. The middle feature of the three for the (3-1) and (3-3) transitions of Fig. 5(b), for example, peaks at ~395.91 and  $\sim 401.48$  nm, respectively, or several cm<sup>-1</sup> to the red of the corresponding Q branch maxima in the molecular spectra [Fig. 5(a)]. Lying still further ( $\sim 2$  Å) to the red is a third feature, apparently associated with high J transitions in the Pbranch. One concludes, therefore, that each of the features in the In\* yield spectrum corresponds to P or Q (and, presumably, R as well)<sup>16</sup> branch transitions of high J. Notice also that, as one would expect, the widths of the three peaks associated with the (3-v'') bands increase according to the  $R \rightarrow Q \rightarrow P$  sequence. Although the features are weaker, the same behavior is observed for the (1-0), (2-1), and (2-2)bands of Fig. 5, as well as the (1-4) band of Fig. 4.

The data of Figs. 2-5 provide a ruler with which the dissociation energy of the  $XO^+$  state may be measured. The strong dependence of the  $In(6s^2S_{1/2})$  yield on J reflects the fact that, as the pump wavelength is decreased, higher rotational energies are required to provide the energy necessary to access the  $In(6^{2}S_{1/2}) + I$  exit channel. It is no surprise, therefore, that the features in the atomic excitation spectrum become increasingly narrow as the pump wavelength moves to the red. Therefore, an examination of the  $In(6 {}^{2}S_{1/2})$  excitation spectra at higher resolution allows one the opportunity to determine the  $XO_g^+$  dissociation energy to within the ground-state vibrational energy ( $\omega_{eX} \cong 177 \text{ cm}^{-1}$ ).<sup>10,11</sup> Figure 6 shows the atomic  $6 {}^{2}S_{1/2}$  excitation spectrum recorded in the 402-411 nm region with a dye laser resolution of 0.1  $cm^{-1}$  and a peak intensity more than an order of magnitude lower than that for the data of Figs. 2–5. Both A-X and B-X transitions lie in this spectral interval, but all of the peaks in Fig. 6 are attributable to  $B \leftarrow X$  bands. Several A  $\leftarrow X$  bands<sup>5,9</sup> also appear in the In(6  ${}^{2}S_{1/2}$ ) yield spectrum, but only as suppressions. A few of these are indicated by asterisks in Fig. 6. Several of the  $B \leftarrow X$  bands identifiable in Fig. 6 are also labeled.

FIG. 7. Partial energy level diagram for InI illustrating the sequential absorption of two pump photons when  $AO^+$  is the intermediate state. The limits for production of  $In(6s\ ^2S_{1/2})$  and ion pairs  $(In^+-I^-)$  by photodissociation of InI are also shown. For convenience, the *X*, *A*, and *B* states are represented by Morse potentials and the spectroscopic constants of Refs. 5 and 11. The lowest horizontal dashed line represents the separated atom limit for the  $XO^+$  state.

An upper limit for the ground  $(XO^+)$  dissociation energy can be estimated by noting that the  $B \leftarrow X(0-2)$  transition is clearly present in the  $In(6 {}^{2}S_{1/2})$  yield spectrum, but the (1-4) band is weak and features attributable to (0-3)transitions are absent, despite the fact that the (1-3), (2-4), and (2-5) bands are strong. Consider first the partial energy level diagram for InI illustrated in Fig. 7. The X, A, and B states are represented by Morse potentials for which the spectroscopic constants are taken to be those of Refs. 5 and 11. Although Rydberg-Klein-Rees (RKR) potentials are also available (Ref. 11), Morse potentials are more than adequate for illustrative purposes. The C1 state is assumed to be a Born potential and the limits associated with the production of  $In(6s^2S_{1/2}) + I$  and  $In^+ - I^-$  ion pairs (Ref. 13) are also shown. Since the energy available to access the neutral exit channel  $In(6^{2}S) + I$  is twice the photon energy plus G(X,v''), then estimating  $D_{e}(X)$  is straightforward. For the key  $(B \leftarrow X)$  vibrational transitions of Fig. 6, the energies available for photodissociation when exciting that particular transition are ordered as (3-5) > (2-4) > (1-3) > (2-5)>(0-2)>(1-4)>(0-3). In other words, the sequential absorption of two photons via the  $B \leftarrow X(1-3)$  transition terminates at a slightly higher energy than does pumping the  $B \leftarrow X(0-2)$  band. Therefore, the strength of the features in Fig. 6 attributed to the  $B \leftarrow X(1-3)$  and (2-5) transitions and the weakness of the (0-2) and (1-4) features suggest that the total energy available when driving the (0-2) band is immediately above the energy threshold for accessing





FIG. 8. Absorption (a) and photoionization spectra for InI in the 395–402 nm region. The photoionization spectrum has not been corrected for the variation of dye laser pulse energy with wavelength.

the  $In(6^{2}S_{1/2})+I$  photodissociation limit. Consequently, the dissociation energy  $D_e(XO^+) < 2\tilde{v}_{(0-2)} + G(v''=2)$  $-\tilde{v}_{In(6^{2}S_{1/2})} = 25\,429\,\mathrm{cm}^{-1}$ , where  $\tilde{v}_{(0-2)}$  is taken to be the peak of the *P* branch and the  $In(6^{2}S_{1/2})$  state lies at 24 373 cm<sup>-1</sup>. It should be mentioned that, although this simple expression ignores the potential barrier associated with the dissociative  $In(6^{2}S_{1/2}) + I(^{2}P_{3/2})$  potential [i.e.,  $V(R_{eX})$  $-V(\infty)$ ], the upper limit is, nevertheless, valid. Also, this value for  $D_e(X)$  is remarkably close to the lower of the two values proposed by Vempati and Jones<sup>11</sup> and will be discussed in more detail in the next section. Similarly, in view of the fact that features associated with the B(0-3) transition are either extremely weak or not present in Figs. 2 and 6, the *lower* limit for  $D_e$  is calculated to be 25 253 cm<sup>-1</sup>. On the basis of these considerations, we conclude that  $D_e(X)$  $= 25\,340 \pm 90\,\mathrm{cm}^{-1}$ .

Before leaving the excitation spectra, it should be mentioned that seven previously unreported  $B \leftarrow X$  bands [(3,0), (4,0), (4,1), (5,1), (5,2), (6,2) and (6,3)] have been observed in these experiments, and several are identified in Fig. 3. The position of each bandhead is consistent with the X and B molecular constants of Refs. 10 and 11. No bands for which v' > 6 were observed in the present work or Ref. 5, which suggests the possibility that higher B(1) vibrational states are predissociated.

## **B.** Photoionization spectra

Although Hälg<sup>17</sup> reported the photoionization of InI in 1943 and Geohegan *et al.*<sup>13</sup> studied by microwave techniques the In<sup>+</sup>–I<sup>-</sup> ion pair yield resulting from the absorption by InI of a single 6.4 eV ( $\lambda$ =193 nm) photon, the photoionization spectra of the molecule have, to our knowledge, not been explored previously. In these experiments, measurements of the relative negative charge collected by the proportional counter (cylindrical diode) were made as the laser wavelength was tuned between 395 and 431 nm. As illustrated in Fig. 8, photoionization spectra recorded in the 395–402 nm region generally replicate the InI absorption spectrum. Band shading and structure are essentially identi-



FIG. 9. Comparison of the relative photoionization and  $\ln(6^{2}S_{1/2})$  yields between 404.0 and 405.5 nm showing the enhancement in photoion production yield associated with A - X(2,0) transitions. The location of the threshold for photodetachment of I<sup>-</sup> is also indicated. It should also be noted that the ionization spectrum is saturated; the resonances associated with A - X(2,0) transitions are, in reality, more than an order of magnitude stronger than any other feature in the photoionization spectrum.

cal to the absorption band profiles in this spectral region and, in particular, the sharply peaked structures corresponding to large *J* that were observed in the  $\ln(6 \, {}^2S_{1/2})$  yield spectra are absent in the photoionization spectrum. At longer wavelengths (403–411 nm), A-X bands are now present and the  $\Delta v = +1, +2$  sequences are dominant.

The most interesting features in the photoionization spectra are structures corresponding to the P branch of the A-X(2-0) transition that lie at 404.5 and 404.8 nm. The ionization current produced at these wavelengths exceeded that produced elsewhere by more than an order of magnitude. Figure 9 presents a comparison of the  $In(6 {}^{2}S_{1/2})$  yield and photoionization spectra in the 404-405.5 nm interval. It should first be noted that, because the photoionization spectrum has intentionally been saturated, the features lying at wavelengths below the  $I^-$  photodetachment threshold at  $\boldsymbol{\lambda}$  $\sim$  405.2 nm (Ref. 18) are considerably stronger than is implied by Fig. 9. Because of the dependence of the cylindrical diode current on particle mobility, the diode response to electrons is greater than that for anions such as I<sup>-</sup> and, therefore, the experiment is considerably more sensitive to the A-X(2,0) resonances than the A-X(3-1) feature, despite the fact that the absorption cross section is approximately the same for both vibrational transitions.

Of particular interest, however, is the lack of correspondence between features in both spectra of Fig. 9. All of the prominent features in the photoionization spectrum are associated with A-X(2-0) and (3-1) transitions, and the notation for labeling the bandheads is adopted from Wehrli and Miescher.<sup>1,19</sup> Several of the weaker peaks in the photoionization spectrum near 405 nm may arise from the *B*   $\rightarrow X(0-2)$  band but, in general, the In<sup>+</sup>-I<sup>-</sup> pair yield shows little influence from  $B \rightarrow X$  transitions. In the same vein, the  $In(6^{2}S_{1/2})$  yield spectrum exhibits virtually no structure assignable to A - X transitions. One concludes, therefore, that, in the spectral region studied here, A-X transitions offer insufficient energy to photodissociate InI (yielding the  $In(6s^2S_{1/2})$  species) but metal-halide ion pairs are produced, whereas the opposite is true if one drives  $B \leftarrow X$  transitions. When exciting  $B \leftarrow X(v' - v'')$  bands in the 395–410 nm region, production of  $In(6s^2S_{1/2})$  predominates over the formation of ion pairs. Since the excitation of the A - X(2,0)transition produces  $In^+ - I^-$  ion pairs but not the neutral species  $In(6^{2}S)$ , one readily finds that the *lower limit* for the  $XO^+$  dissociation energy is ~25 143 cm<sup>-1</sup>. This estimate is  $\sim 100 \text{ cm}^{-1}$  smaller than, but consistent with, the lower limit suggested in the last section.

The value for  $D_e$  proposed here,  $25340\pm90 \text{ cm}^{-1}$ , agrees well with the estimate by Vempati and Jones<sup>11</sup> of  $D_0(XO^+) = 25296 \text{ cm}^{-1}$ , assuming the InI ground state to be covalently bonded and the AO<sup>+</sup>, B1, and C1 states are derived from  $\ln({}^2P_{3/2}) + I({}^2P_{3/2})$ . As discussed in Ref. 11, this value for the XO<sup>+</sup> dissociation energy is consistent with measurements from flame photometry (~25880 cm<sup>-1</sup>, Ref. 8), the upper limit of 27630 cm<sup>-1</sup> determined from photoionization experiments (Ref. 7), and the range in values proposed in Ref. 1 (21700–27430 cm<sup>-1</sup>). It should also be noted that the estimates of  $D_0(X)$  by Vempati and Jones<sup>11</sup> were drawn from Morse potential extrapolations and, as the authors mention, "...should be considered as upper limits."

### C. Fluorescence suppression spectra: ${}^{2}S_{1/2}$ , ${}^{2}P_{1/2,3/2}$ , ${}^{2}D_{3/2,5/2}$ $\leftarrow 6 s \, {}^{2}S_{1/2}$ transitions of In

For excitation wavelengths beyond ~410 nm, populating the 6  ${}^{2}S_{1/2}$  state of In from InI requires the absorption of three photons. Since the threshold wavelength for photoionization of the  $6s^2S_{1/2}$  level by two photons of equal energy is 448 nm, excitation spectroscopy of  $In(6s^{2}S_{1/2})$  in the  $\lambda$ >448 nm region is a convenient tool for examining high Rydberg states of atomic In while simultaneously probing  $In(6s^2S_{1/2})$  production. Figure 10 shows the fluorescence suppression spectrum for indium in the 450-470 nm region that was recorded by monitoring  $6s^2S_{1/2} \rightarrow 5p^2P_{1/2}$  emission at 410.2 nm. The strongest features correspond to the dipole-allowed  $np^2 P_{1/2,3/2} \leftarrow 6s^2 S_{1/2}$  transitions, and principal quantum numbers  $n \ge 25$  are readily observable. Also, the fine structure splitting in the  ${}^{2}P$  states has not been reported previously for the n=15-17 terms of the series, but the values measured in these experiments (shown in Fig. 10) are in agreement with the expression given by Neijzen and Dönszelmann:<sup>20</sup>  $\Delta T_n = 5880n^{*-3}$  (in cm<sup>-1</sup>), where  $\Delta T_n$  is the  ${}^{2}P_{1/2-3/2}$  splitting and  $n^{*}$  is the effective quantum number.

Also noticeable in Fig. 10 are single-photon transitions terminating on the  $ns^{2}S_{1/2}$  ( $15 \le n \le 25$ ) and  $md^{2}D_{3/2,5/2}$  ( $13 \le m \le 25$ ) states of the atom. These transitions were found to quickly vanish as the laser pulse energy was decreased, but were observed for principal quantum numbers as low as m=9. The spectrum of Fig. 10 is reminiscent of the



FIG. 10. Fluorescence suppression spectrum of  $\ln(ns^2S_{1/2}np^2P_{1/2,3/2},nd^2D_{3/2,5/2} \leftarrow 6s^2S_{1/2}, 25 \leq n \leq 15)$  transitions obtained by monitoring  $\ln(6^2S_{1/2} \rightarrow 5^2P_{1/2})$  spontaneous emission at 410.2 nm. In this wavelength region, production of the  $6^2S_{1/2}$  state requires the absorption of three photons.

multiphoton ionization spectrum of the Column III B alkyls Al<sub>2</sub>(CH<sub>3</sub>)<sub>6</sub>, Ga(CH<sub>3</sub>)<sub>3</sub>, and In(CH<sub>3</sub>)<sub>3</sub> that were reported by Hackett, John, and Mitchell,<sup>21–23</sup> who demonstrated that the absorption of 4–6 photons in the visible completely removes the methyl ligands and yields a metal ion. Thus, the multiphonon ionization (MPI) spectrum of the alkyl in the visible has the signature of solely the metal atom. In the case of In(CH<sub>3</sub>)<sub>3</sub>, two-photon ionization of the In 6  ${}^{2}S_{1/2}$  state, resonantly enhanced by the  $np {}^{2}P_{J}$  states (13 $\leq n \leq 30$ ) was observed<sup>22</sup> but, to our knowledge, the single-photon forbidden,  $md {}^{2}D_{3/2,5/2} \leftarrow 6s {}^{2}S_{1/2}$  transitions have not been reported previously.

### **IV. CONCLUSIONS**

The relative, wavelength-dependent yield of  $In(6s^2S_{1/2})$ from InI, and the InI ground state  $(XO^+)$  dissociation energy have been measured by excitation spectroscopy and laserinduced fluorescence in the spectral region that overlaps the  $AO^+$ ,  $B1 \leftarrow XO^+$  transitions of the molecule (390–431 nm). Seven previously unreported  $B \leftarrow X$  bands have been observed and the absence of vibrational bands for which v'>6 suggests that the B1 state is predissociated. The presence or absence of specific  $A \leftarrow X$  or  $B \leftarrow X$  bands in the  $In(6^{2}S_{1/2})$  excitation spectrum or photoionization spectra permit the  $XO^+$  ground-state dissociation energy to be determined to be  $D_e = 25340 \pm 90 \text{ cm}^{-1}$ , which agrees with the lower value suggested in Ref. 11—the value of  $D_{e}$  to be expected if: (1)  $XO^+$  is covalent, and (2) the  $AO^+$ , B1, and C1 states are all correlated, in the separated atom limit, with  $In(5p^2P_{3/2}) + I(^2P_{3/2})$ . Deducing  $D_e$  from direct spectroscopic evidence, rather than from the extrapolation of a Morse potential vibrational series, yields a value more accurate than those available previously, due in part to the fact that the result proposed here is not dependent upon the structure of the  $XO^+$  state near the dissociation limit. The  $In(6s^{2}S_{1/2})$  relative yield data, particularly in the 395–407 nm region, exhibit a strong dependence upon the B-state rotational quantum number, which reflects the fact that the photodissociation process is near threshold in this spectral region. Fluorescence suppression spectroscopy in the 450– 470 nm region gives the relative  $\ln(6s^2S_{1/2})$  yield and has revealed transitions originating from the  $6s^2S_{1/2}$  state of In and terminating on  $np^2P_{1/2,3/2}$ ,  $ns^2S_{1/2}$ , and  $nd^2D_{3/2,5/2}$ Rydberg states having principal quantum numbers larger than 25. The  $nd, ns \leftarrow {}^2S_{1/2}$  transitions are normally forbidden by L-S coupling selection rules and appear only at the highest pump laser intensities available. Fine structure splitting within the  $np^2P$  states of In (n=15-17) was also observed.

The focus of these experiments is the study of metal– halide diatomic excited-state dynamics and, specifically, the competition between photodissociation, ionization, and molecular fluorescence in energy disposal. To our knowledge, these experiments are the first laser spectroscopic studies of InI, and further experiments in this and structurally similar metal–halides will be necessary to optimize the production of a desired species such as In<sup>+</sup> or In(6s  ${}^{2}S_{1/2}$ ).

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