

Bound-free transitions and the dissociation limit

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Abstract. Following a sequential two-photon excitation, fluorescence is observed from several selectively excited single rotational-vibrational energy levels of the $E^3\pi_0^+$ state of molecular iodine. The re-emitted $E \rightarrow B$ fluorescence spectrum from each of the populated ro-vibrational level of the E state consists of a series of sharp lines terminating on the various discrete ro-vibrational levels of the B state and a few broad lines due to transitions taking place on to the continuum of the B state. The point of transition from sharp lines to broad features in the fluorescence spectrum has been utilized to determine the B state dissociation limit. This method of obtaining the dissociation limit of the molecular electronic states appears to be quite simple and straightforward.

Keywords. Two-photon excitation; bound-free transitions; dissociation energy.

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1. Introduction

The study of bound-free transitions in diatomic molecules had drawn considerable interest recently due to its importance in calculating the unknown potential curve of the involved electronic state (Tellinghuisen 1974; Tamagake and Sester 1977) as well as explaining the observed spectral features (Tellinghuisen 1975, 1984; Golde 1975). The bound-free transitions resulting in broad spectral features originate from the internal diffraction effect, which was first predicted by Condon in 1928 (Condon 1928) but clearly observed only in 1974 (Rousseau and Williams 1974). The phenomenon was studied in $E \rightarrow B$ system of iodine molecule both experimentally (Rousseau and Williams 1974; Brand *et al* 1982) and theoretically (Tellinghuisen 1975). However, the influence of E vibrational levels of different energies on the spectral features does not appear to have been reported so far.

We discuss here the study of spectral features due to transitions originating from several single ro-vibrational levels of the E state in the range of $28 \leq v_E \leq 44$ to the B state continuum of molecular iodine. Furthermore, this study also leads quite easily to the determination of dissociation limit of the intermediate electronic state.

2. Experimental

The constant-energy-difference sequential two-photon photoexcitation technique (Sharma *et al* 1986) is employed to populate the individual rotational-vibrational levels

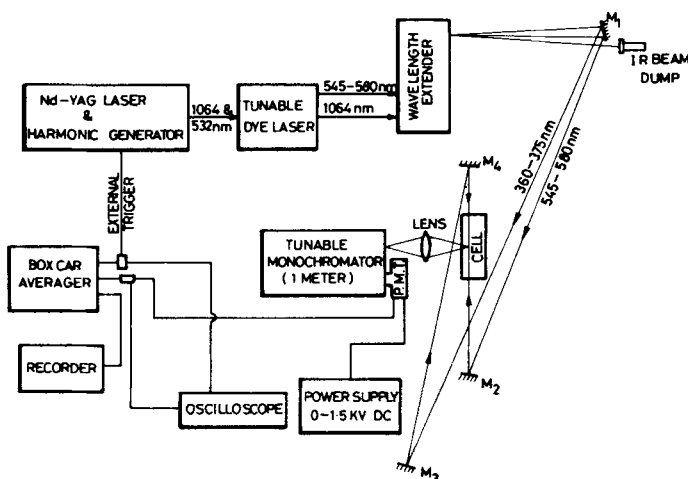


Figure 1. Experimental arrangement for the observation of $E \rightarrow B$ fluorescence near the dissociation limit of the B state of I_2 . The monochromator slits are narrowed as much as possible to distinguish sharp and broad features. By manually tuning the dye laser, the visible and UV photons (which always differ by constant-energy from each other), are selected to excite a particular ro-vibrational level of the E state.

of the E state in iodine molecule. The experimental set-up is essentially the same as described by Sharma *et al* (1986) and shown in figure 1. Briefly the source of tunable two-photon radiation is the Quanta Ray DCR-2A(20) Nd-YAG pulsed laser, the PDL-1 dye laser and the WEX-1 wavelength extender. The second harmonic output of the Nd-YAG laser at 532 nm pumps the tunable dye laser whereas the dye laser output is mixed with the unconverted fundamental at 1064 nm in the WEX to produce the UV output. Therefore the visible and UV outputs are always differing by a constant amount of energy of one IR quanta. The visible output from 545 to 580 nm and the UV output from 360 to 375 nm are obtained by using Rh-590 dye solution. The unused part of the IR radiation is disposed off in a beam dump and the other two beams are passed coaxially from opposite directions through a sealed pyrex cell containing iodine vapour at about 0.25 torr pressure. The visible beam has a pulse width of 6 ns, full width at half maximum (FWHM) of 0.25 cm^{-1} and typical pulse energy of about 20 mJ while the UV radiation is of 8 ns width, 1 cm^{-1} FWHM and about 3 mJ energy per pulse. The laser repetition rate is 20 Hz.

The excitation is achieved by sequential absorption of the visible and the UV photon via the scheme $E^3\pi 0_g^+ \leftarrow B^3\pi 0_u^+ \leftarrow X^1\Sigma_g^+$. The $E \rightarrow B$ fluorescence is focussed into the entrance slit of a monochromator (Monospex 1000) and the signal is detected using a photomultiplier tube (Hamamatsu R446) placed at the exit slit of the monochromator. The signal is processed in a boxcar averager (EG & G model 165/162), triggered externally by a synchronous output of the laser system and recorded on a chart recorder. With a 15 ns gate duration and $10 \mu\text{s}$ time constant, good signal to noise ratio is obtained. For a particular excitation to a single ro-vibrational level of the E state, the monochromator (with a slit width of less than 10 microns) is scanned near the dissociation limit of the B state to record the $E \rightarrow B$ fluorescence spectrum.

3. Results and discussion

Since the two-photons always differ by constant energy and since the transitions have to obey the rotational selection rules, the possibility of two-photon transitions to the E state is drastically reduced. This helps to selectively populate the ro-vibrational levels of the E state when the dye laser is scanned. The selective picking out of a single ro-vibrational level simplifies the re-emission spectrum which facilitates the clear observation of $E \rightarrow B$ bound-free spectral features. The energy ladders involved in the transitions are determined as usual from the reported molecular constants of the states involved (Sharma *et al* 1986).

We have analysed the fluorescence from a number of ro-vibrational levels of the E state near the dissociation limit of the B state. Qualitatively the spectra resulting from each of the transitions have similar pattern—namely a series of sharp lines followed by a few broad lines. As explained schematically in figure 2, the sharp lines result from

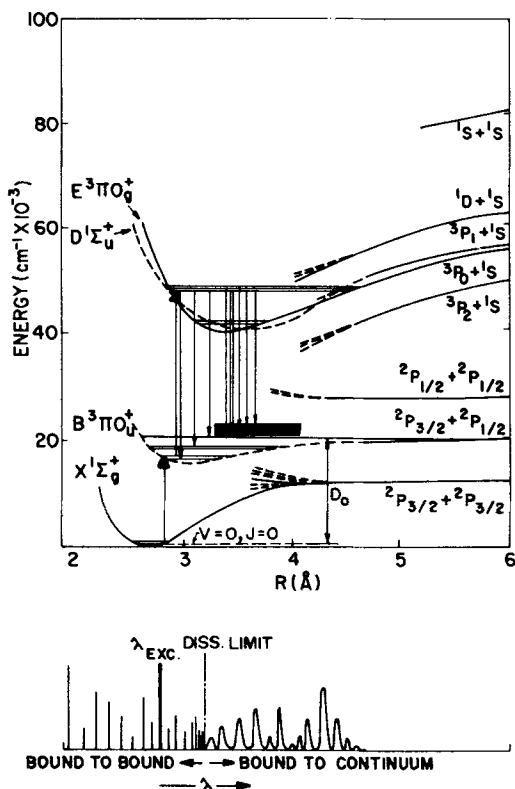


Figure 2. The energy levels of iodine molecule involved in the two-photon excitation. The upward arrows correspond to the absorption of visible and UV radiation and the downward arrows represent the $E \rightarrow B$ fluorescence. The re-emitted radiation terminating on the bound levels of the B state produce sharp lines, whereas the transitions on the continuum result in broad lines. This is indicated schematically at the bottom of the figure. D_0 is the dissociation energy of the B state with respect to $v=0$ and $J=0$ of the X state.

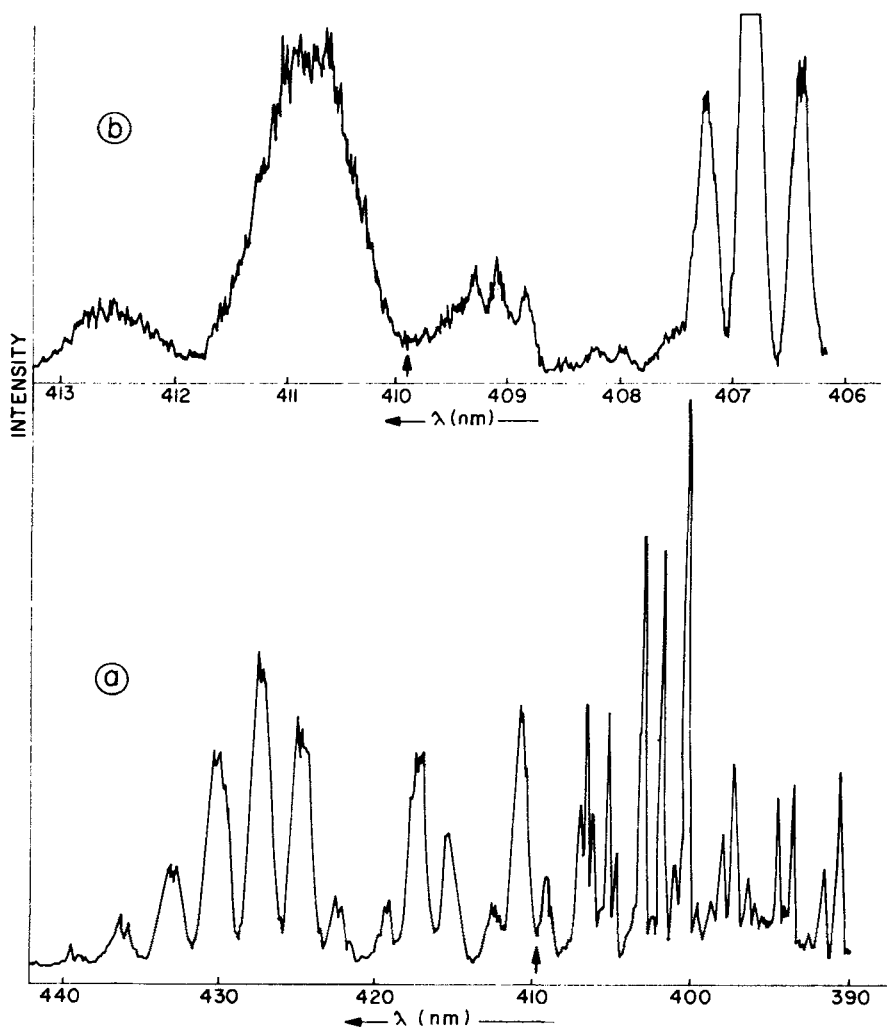


Figure 3. $E \rightarrow B$ fluorescence near the dissociation limit of the B state of I_2 due to the transition $E(32, 51) \leftarrow B(17, 52) \leftarrow X(1, 53)$. The sharp features are due to bound-to-bound transitions. The arrow indicates the end of sharp peaks followed by broad features. The two spectra correspond to the scanning of the monochromator at (a) $50 \text{ \AA}/\text{min}$ and (b) $2.5 \text{ \AA}/\text{min}$.

transitions between the populated level of the E state and various allowed ro-vibrational levels of the B state, whereas the broad features originate when the transitions take place to the continuum of the B state. As an example for the transition $E^3\pi 0_g^+(v' = 32, J' = 51) \leftarrow B^3\pi 0_u^+(v^i = 17, J^i = 52) \leftarrow X^1\Sigma_g^+(v'' = 1, J'' = 53)$, the corresponding $E \rightarrow B$ fluorescence spectrum near the dissociation limit of the B state is shown in figure 3.

The nature of the broad spectral pattern has been explained by various authors (Mulliken 1971; Golde 1975; Tellinghuisen 1975; Tamagake and Sester 1977). Such spectra occur for the transitions in which the molecule is vibrationally unbound in at

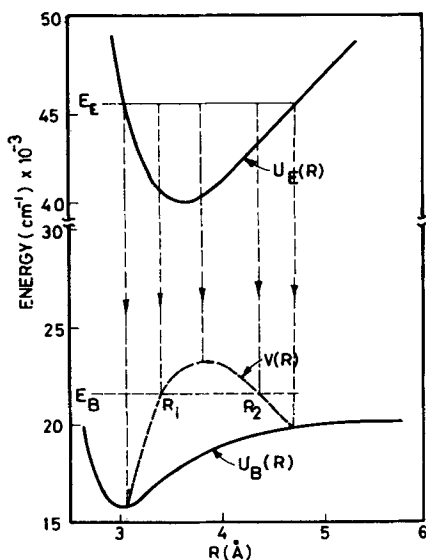


Figure 4. Potential energy curves for the E and B electronic states of I_2 . The dashed curve is the difference potential, $V(R) = E_E - U_E(R) + U_B(R)$. R_1 and R_2 are points of stationary phase for unbound B state of energy E_B for which the major contribution to the overlap takes place.

least one of the two electronic states involved. The broad band structure results from the variation of the Franck-Condon (FC) overlap factors between the discrete and continuum wave functions. Interpreted classically the FC principle dictates that the emission terminates on the curve, $V(R) = E_E - U_E(R) + U_B(R)$, where $V(R)$, a function of internuclear distance R , is the difference potential, E_E is the energy of the bound level in the E state, $U_E(R)$ and $U_B(R)$ are the potential energies of the E and B states respectively. $V(R)$ is the locus of the points which conserve nuclear position and momentum in the transitions as shown in figure 4. Franck-Condon distributions to the various energies in the continuum can be categorized as displaying reflection structure or interference structure. Reflection structure is the case where the spectrum reflects the radial probability distribution in the initial state i.e., it conserves peak and node count. Semiclassical theory (Tellinghuisen 1975, 1984) shows that reflection structure occurs when the difference potential is monotonic in the region sampled by the initial wavefunction ψ_{ν} , and interference structure occurs when ψ_{ν} samples a polytonic $V(R)$, i.e. a region where two or more points of stationary phase occur for a given energy of the final state.

In iodine molecule, the E state ($R_e = 3.65 \text{ \AA}$) is situated at larger internuclear distance relative to the B state ($R_e = 3.06 \text{ \AA}$). The construction of difference potential due to transitions from a bound state of relevant energy shows its polytonic behaviour as illustrated in figure 4. For a given unbound B state energy E_B the major contribution (Mulliken 1971) to the overlap occurs near R —the root of $V(R) = E_B$ where the vibrational wavefunctions of the E and B states have the same periodicity. In addition, if the two wavefunctions are in phase, a spectral peak occurs at frequency $\nu = (E_E - E_B)/h$. For unbound B state levels which lie below the extremum $V_{\max}(R)$, the two regions of R namely R_1 and R_2 contribute significantly to the overlap. These

contributions may add constructively or destructively and result in the characteristic modulated frequency pattern as found in the $E \rightarrow B$ spectrum (figure 3).

In our experiment, we are able to excite the ro-vibrational levels in the E state between $28 \leq v_E \leq 44$. Although the region covered is narrow, the effect of higher energy ro-vibrational levels as compared to the lower energy levels on the broad spectral pattern is clearly observable. Although the overall pattern remains the same,

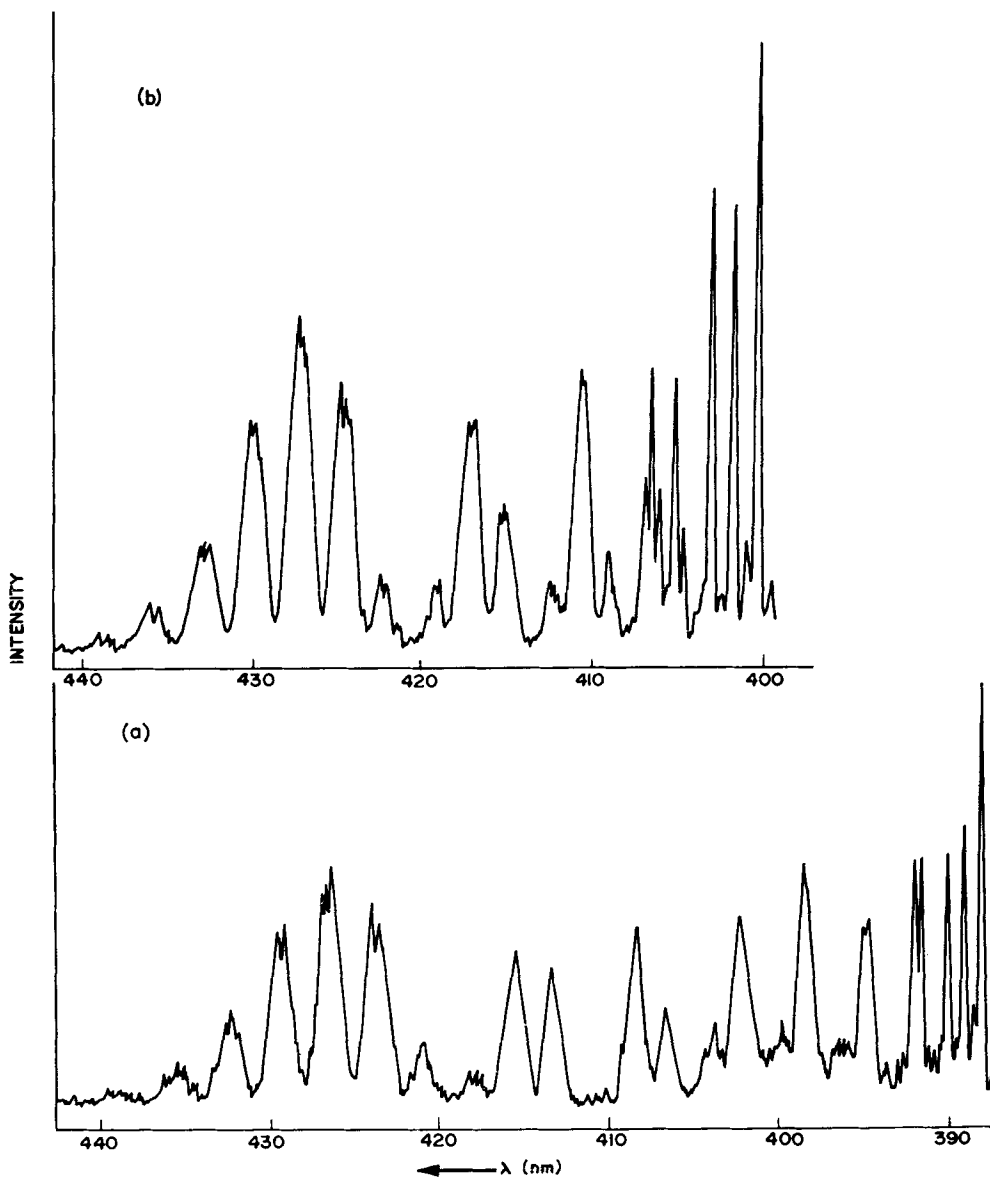


Figure 5. $E \rightarrow B$ fluorescence spectra near the B state dissociation limit originating from $v_E = 42$ and 32 of I_2 . The two spectra result due to the sequential two-photon absorption (a) $E(42, 96) \leftarrow B(22, 97) \leftarrow X(1, 98)$ and (b) $E(32, 51) \leftarrow B(17, 52) \leftarrow X(1, 53)$. The spectrum from $v_E = 42$ shows 19 broad lines whereas $v_E = 32$ shows only 12.

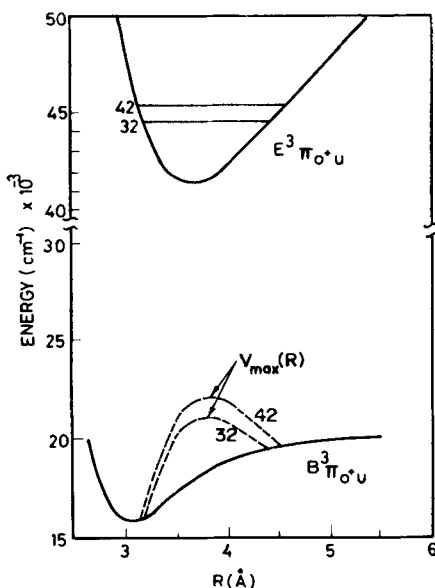


Figure 6. Construction of two difference potentials for $v_E=42$ and 32. As E_E increases, the maximum of difference potential is shifted by the same amount so that the difference between E_E and the corresponding $V_{\max}(R)$ remains constant. Thus the lowest observable transition frequency is independent of E_E . Transitions from higher E_E hence sample larger regions of the continuum.

the spectra originating from higher energy ro-vibrational levels reveal larger number of broad lines than that from lower energy levels. This is illustrated by the two observed spectra originating from $v_E=42$ and 32 as shown in figure 5. The additional features appear at the beginning of the continuum. As E_E increases, the additional upper regions of the B state continuum become available for difference potential as illustrated in figure 6. Thus the continuum region sampled by $\psi_{v'}$ increases with E_E . The minimum transition frequency possible at the extremum of difference potential does not depend on the position of the ro-vibrational level of the E state since the difference of E_E and extremum of the corresponding difference potential always remains the same. Around the maximum of difference potential, the transition frequency which involves the initial wavefunction having maximum momentum, displays strongest intensity of broad features. The possibility of strong transition probability as a function of frequency can occur corresponding to the R values where nuclei in the initial state have maximum kinetic energy (Mulliken 1971).

4. Dissociation energy

The very high density of vibrational levels near the dissociation limit in the electronic states of heavy molecules makes it difficult to determine the dissociation energy by conventional means. Most estimates of the dissociation energy come from extrapolation formula which requires assumptions about the form of potential at large-internuclear distances. By selectively exciting discrete ro-vibrational levels close to the

Table 1. Determination of dissociation limit of B state of molecular iodine.

Transition	$\bar{\nu}_{B-X}$ (cm^{-1})	$\bar{\nu}_{E-B}$ (cm^{-1})	$\bar{\nu}_C$ (cm^{-1})	$\bar{\nu}_X$ (cm^{-1})	D' (cm^{-1})	D_0 (cal.) (cm^{-1}) average
$E(32, 73) \leftarrow B(17, 74) \leftarrow X(1, 73)$	17342.13	26736.70	24447.9	413.95	20044.9	
$E(32, 51) \leftarrow B(17, 52) \leftarrow X(1, 53)$	17364.33	26759.05	24401.0	319.57	20041.9	
$E(34, 101) \leftarrow B(17, 100) \leftarrow X(0, 101)$	17490.00	26884.57	24718.8	383.75	20039.5	20042.6
$E(42, 96) \leftarrow B(22, 97) \leftarrow X(1, 98)$	17731.22	27125.79	25386.4	573.60	20044.2	

Here D' is given by $D' = (\bar{\nu}_X + \bar{\nu}_{B-X} + \bar{\nu}_{E-B}) - \bar{\nu}_C$.
(The value reported in literature is $D_0 = 20043.21 \text{ cm}^{-1}$)

dissociation limit and through enhanced detection sensitivity by two-photon technique, a direct method of observing the dissociation limit has been reported (Danyluk and King 1976). We report here an alternative approach based on the observation of bound-to-bound and bound-to-free transitions for the determination of the dissociation limit of the excited electronic state in a much simpler way.

The change of spectral pattern from sharp to broad features indicates the beginning of the continuum. But the transition probability to the bound B state levels may reduce drastically for some transitions as the continuum is approached. Further the transitions themselves may not be allowed after a certain value of v_B by the J selection rules especially for higher J states. In the excitation schemes employed here, due to small values of Franck-Condon factors and also the crowding of ro-vibrational levels near the dissociation limit, the last sharp transitions are weak and poorly resolved. Consequently at the onset of continuum the change of spectral pattern from sharp to broad features may not be distinct. But as seen in figures 3 and 7, the first broad feature is quite distinguishable and therefore can easily be located. The point of change appears to be at the end of the last bound ro-vibrational levels and the beginning of first broad feature. This is confirmed from the known value of dissociation limit of the B state of molecular iodine. Therefore one may get a fairly good idea of the dissociation limit of the B state of molecular iodine from this observation directly.

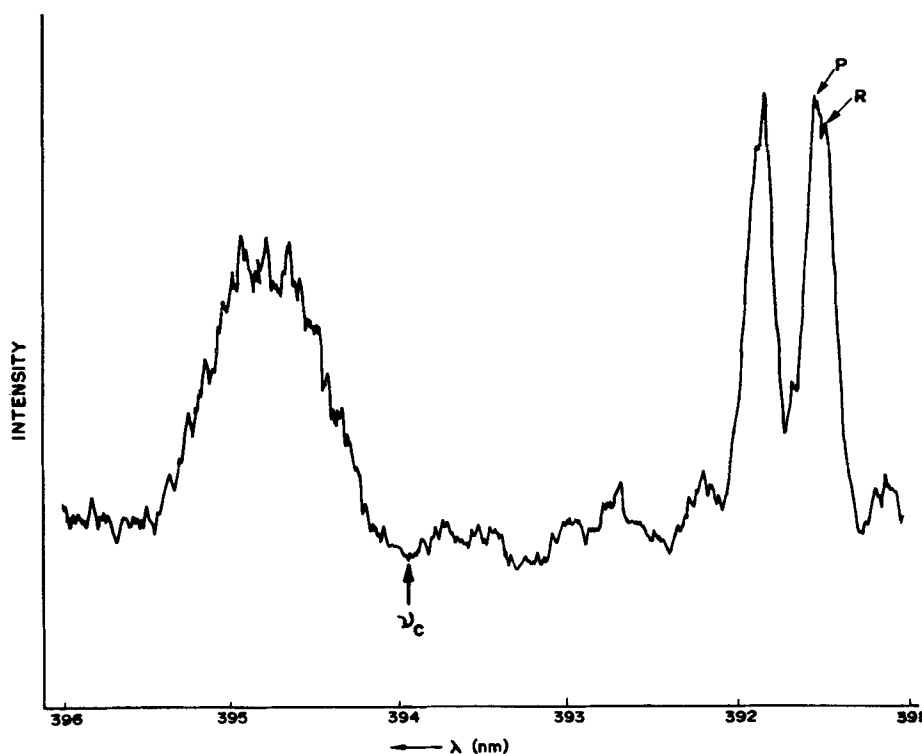


Figure 7. $E \rightarrow B$ fluorescence spectrum from $E(42,96) \leftarrow B(22,97) \leftarrow X(1,98)$ absorption near the dissociation limit at expanded scale. Each sharp peak consists of P and R branch rotational lines. The arrow indicates the position of the transition point taken as $\bar{\nu}_c$ for the purpose of calculation of D_0 .

The dissociation limit, D_0 of the B state with respect to $v = 0$ and $J = 0$ of the X state can be calculated from the $E - B$ fluorescence spectra of a few observed transitions. This is shown in table 1. To illustrate the calculations involved, we take the example of fluorescence observed from the $E(42, 96) \leftarrow B(22, 97) \leftarrow X(1, 98)$ excitation scheme. The excitation energy required for $B \leftarrow X$ transition in this case is $\bar{\nu}_{B-X} = 17731.22 \text{ cm}^{-1}$ and for $E \leftarrow B$ transition is $\bar{\nu}_{E-B} = 27125.79 \text{ cm}^{-1}$. The onset of continuum occurs after the last bound-to-bound transition or just before the first observable broad feature at 393.91 nm i.e. $\bar{\nu}_C = 25386.40 \text{ cm}^{-1}$ as shown by the arrow in figure 7. The dissociation limit is thus given by $D' = (\bar{\nu}_X + \bar{\nu}_{B-X} + \bar{\nu}_{E-B}) - \bar{\nu}_C$, here $\bar{\nu}_X$ is the energy of the X state with respect to $v = 0$ and $J = 0$ which is given in this specific case by

$$\bar{\nu}_X(1, 98) = 573.60 \text{ cm}^{-1}.$$

Thus the dissociation limit of the B state is calculated as

$$D' = (573.60 + 17731.22 + 27125.79) - 25386.40 = 20044.2 \text{ cm}^{-1}.$$

Similar calculations for $E(32, 51) \leftarrow B(17, 52) \leftarrow X(1, 53)$ excitation give $D' = 20041.9 \text{ cm}^{-1}$. By looking similarly at some other $E - B$ fluorescences one can obtain a few consistent values of D' . The average of these D' values can be taken as the value of the dissociation limit D_0 . In our calculations, the dissociation limit thus obtained is within a wavenumber of the reported value in literature (Danyluk and King 1976).

The technique of determining the dissociation limit of excited electronic state discussed here, requires only the knowledge of rotational constant (B_e) of the ground electronic state for the purpose of calculating the rotational contribution to the energy of the initial ro-vibrational level $\bar{\nu}_X$. All other parameters used to obtain D' can be determined from the observed spectra itself. To elaborate the point, as the monochromator is scanned to record $E \rightarrow B$ fluorescence for a particular excitation, the values of $\bar{\nu}_{E-B}$ and $\bar{\nu}_C$, which are UV excitation line and the transition point from sharp to broad features respectively, can be easily determined from the spectrum. Similarly, the observation of $B \rightarrow X$ fluorescence near the anti-Stokes side of the visible excitation line can be utilized to obtain $\bar{\nu}_{B-X}$ which is the position of excitation line itself. Even otherwise $\bar{\nu}_{B-X}$ is equal to $\bar{\nu}_{E-B} - IR$. Further the vibrational contribution to the value of $\bar{\nu}_X$ can be obtained by calculating the separation of last anti-Stokes line from the visible exciting line. Zero-point energy contribution, $(1/2)\omega_e$ to $\bar{\nu}_X$ can be evaluated from the separation of the last two anti-Stokes lines in order to arrive at D_e which is given as $D_e = D_0 + (1/2)\omega_e$. In each vibrational transition, separation of the rotational components (here P and R lines) can give an idea of the J assignment of the ground state. Therefore only the rotational parameter B_e remains the unknown factor. Thus provided the rotational constants of the ground state are known, this technique emerges as self sufficient to determine the dissociation limit of the excited electronic state. However the ground state value of B_e is known for many simple molecules. If absolutely nothing is known about a certain molecule, the dissociation limit obtained by this technique will be reduced only to the extent of rotational contribution to $\bar{\nu}_X$ which is not very large at most times.

This method of arriving at the dissociation limit of an electronic state whose value has not been known so far, therefore, appears to be direct and quite promising.

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