Final Technical Report

NASA Grant NGR 05-018-065

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Jan. 12, 1971

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Research which was conducted in whole or in part under NASA Grant NGR 05-018-065 and which has resulted in published articles is listed in the following list of publications:

" Intensity Measurements in the $B^3\Pi - X^1\Sigma$ system of I_2." Ara Chutjian and Thomas C. James J. Chem. Phys. 51, 1242 (1969) . A70-13298

"Intensity of the Quadrupole Rotation-Vibration Spectrum of Molecular Hydrogen". Thomas C. James J. Mol. Spectry. 32, 512, (1969) . A70-19366

"Calculations of Collision Narrowing of the Quadrupole Lines in Molecular Hydrogen." Thomas C. James J. Opt. Soc. Am. 59, 1602 (1969) .

"Calculation of Predissociation Rates of the $B^3\Pi$ State of I_2 ." Ara Chutjian, J. Chem. Phys. 51, 5414, (1969).

" Curves of Growth of Autoionizing Spectral Lines with Application to the 3s-4p Transition in Argon." Ara Chutjian and Robert W. Carlson J. Opt. Soc. Am. 60, 1204 (1970).

A70-41931

Five copies of each of the above articles are enclosed. A brief summary of the contents of each article is given further on in this summary.

People who received financial support from the present grant were:

Thomas C. James --principal investigator -- summer salary

Ara Chutjian -- Postdoctoral associate -- approximately 20 months

Walter Lee -- technician -- half salary for three months.

Summary of Published articles:

The first paper in the above list , having to do with intensity measurements on I_2, was concerned with the measurement of equivalent widths of a number of rotational lines in different vibronic bands of the $B^3\Pi - X^1\Sigma$ transition of I_2. These equivalent widths are converted to line intensities using a Doppler curve of Growth. This curve of growth is presented in a table as an aid to other investigators who wish to study intensities of Doppler shaped lines.

The most important result of the I_2 intensity study was that it permitted us to calculate a reliable value for the radiative lifetime of I_2. Since there were a number of different values for this quantity as measured by several investigators, an accurate value from absorption intensities was desireable. A comparison of our radiative lifetime with total lifetimes as measured directly showed that the actual lifetime was less than the radiative lifetime. The difference was found to increase with increasing vibrational excitation of the B state and was attributed to predissociation. The state causing the predissociation is the $A\,{}^1\Pi$ state which is a repulsive potential which runs parallel to the inner turning points of the B state. The comparison of the actual and radiative lifetimes provides one of the few existing quantitative measurements of a rate of predissociation.

The logical extension of this study is reported in the fourth paper in the above list; the one having to do with calculation of predissociation rates. In this study overlap integrals between wavefunctions for the bound vibrational levels of the B state and the continuum functions of the repulsive A state were evaluated. By adjusting the position of the repulsive potential it was possible to account for the relative rates of predissociation of the vibrational levels of the B state. From these calculations it was possible to extract a value for the electronic matrix element of the perturbation operator causing the predissociation.

The value of the above two articles is that they demonstrate the value of quantitative studies of predissociation in in determining the positions of repulsive potential curves, and also they demonstrate the quantitative application of Kronig's theory of predissociation to diatomic molecules.

The second of the above listed papers presents a calculation of all of the quadrupole moment matrix elements which are likely to be of interest in astrophysical studies of the intensity of the quadrupole spectrum. Values of these matrix elements are given for the pure rotation spectrum and for vibrational bands from the 1-0 band thru the 4-0 band.

The paper on calculations of collision narrowing of the quadrupole spectrum of hydrogen is a numerical application of Galatry's theory of collision narrowing. The results are used to obtain a value for the pressure broadening coefficient of hydrogen from Rank's reported equivalent width measurements. A significant feature of this article is that it shows that the expression of Galatry can be reduced to a simple form which makes calculations easy to carry out. The analysis of Rank's data shows the Galatry theory to be adequate for describing equivalent width measurements and therefore provides a dependable method for calculating curves of growth to interpret various astronomical equivalent width measurements.

The combination of this and the previous paper provide the basic information required to attempt to interpret equivalent width measurements in terms of a total abundance and effective pressure of hydrogen atmospheres.

The last of the above papers on curves of growth of autoionizing transitions applies the usual curve-of-growth technique to lines having the unusual shape characteristic of transitions to a bound level which is imbedded in a continuum with which it interacts. Since these lines appear as apparent emission features on a continuum absorption, the curve-of-growth has a qualitatively different form from the more usual absorption curves of growth. It is shown that equivalent width measurements can yield valuable information about the intensity and shape of such lines even in cases where resolution is insufficient to resolve the true line shape.

Reprinted from JOURNAL OF MOLECULAR SPECTROSCOPY, Volume 32, No. 3, December 1969

Intensity of the Quadrupole Rotation-Vibration Spectrum of Molecular Hydrogen

In a recent article Karl and Poll (*4*) report calculations of the quadrupole moment matrix elements for a number of lines in the rotation–vibration spectrum of hydrogen. These calculations were carried out using numerical solutions of the vibrational wave equation combined with the theoretical quadrupole moment calculated by Kolos and Wolniewicz (*6*). Their calculations are in good agreement with the experimental measurements of Fink *et al.* (*1*) which suggests that the theoretical results are quite reliable. In view of the astrophysical interest in the 4–0 $S(1)$ line it seemed worthwhile to carry out the calculation for this line as this was not reported in the paper by Karl and Poll. In addition to the 4–0 $S(1)$ line, there is considerable interest in knowing the relative intensities of many other lines in the spectrum due to the possibility of observing clouds of interstellar hydrogen from absorption or emission studies. We thus report values of vibrational matrix elements for Q, O, and S lines for all the bands of hydrogen from the 0–0 (pure rotational) band through the 4–0 band.

TABLE I

MATRIX ELEMENTS $\langle V'J'|\, N(r)\, |V''J''\rangle$ FOR H_2 (Debye–angstroms)

Line	Band				
	0–0	1–0	2–0	3–0	4–0
$Q(0)$	0.64672	0.11742	−0.01552	0.00237	0.00046
$Q(1)$	0.64826	0.11751	−0.01557	0.00238	0.00046
$Q(2)$	0.65132	0.11769	−0.01565	0.00240	0.00047
$Q(3)$	0.65591	0.11796	−0.01579	0.00243	0.00048
$S(0)$	0.64889	0.10460	−0.01611	0.00283	0.00064
$S(1)$	0.65174	0.09617	−0.01633	0.00310	0.00075
$S(2)$	0.65599	0.08784	−0.01644	0.00335	0.00087
$S(3)$	0.66164	0.07963	−0.01643	0.00357	0.00096
$O(2)$	—	0.13054	−0.01471	0.00188	0.00028
$O(3)$	—	0.13937	−0.01404	0.00154	—
$O(4)$	—	0.14828	−0.01327	0.00119	—

The calculation was done in the manner described previously by James (*3*) but differs in that the theoretical quadrupole moment calculated by Kolos and Wolniewicz extends from 0.2 to 2 Å, i.e., well beyond the range of internuclear distance between the turning points for the $v = 4$ vibration, which lie at approximately 0.49 and 1.32 Å. The previous calculation [James (*3*)] used the theoretical result of Kolos and Roothaan (*5*) which did not cover a sufficiently wide range of internuclear distance for reliable calculations of the quadrupole line intensities of the higher overtones.

The calculated values of the quadrupole matrix elements are given in Table I. The absorption intensities can be calculated from the expression given in our earlier paper [James (*3*)]:

$$I(\text{cm}^{-1}/\text{cm amagat}) = 3.316 \times 10^{-15} X_{V''J''}\sigma^3 \mid \langle v' \mid N(r) \mid v'' \rangle \mid {}^2 S_{J'}^{J''}.$$

It is of some interest to look at the relative intensity of the 3–0 and 4–0 $S(1)$ line using these new results. The intensities can be calculated to be I (3–0) = 0.00154 cm^{-1}/*km-amagat* and I (4–0) = 0.000192 cm^{-1}/km-amagat. Thus the 3–0 $S(1)$ line is expected to be about 8 times as intense as the 4–0 $S(1)$ line. The 4–0 $S(1)$ line is weaker than suggested by James (*3*) and is more nearly equal to the value suggested by Rank and Associates [Fink *et al.* (*1*) and Foltz and Rank (*2*)].

ACKNOWLEDGMENT

The support of the National Aeronautics and Space Administration is gratefully acknowledged.

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Received: April 1, 1969

Reprinted from THE JOURNAL OF CHEMICAL PHYSICS, Vol. 51, No. 12, 5414–5419, 15 December 1969
Printed in U. S. A.

Calculation of Predissociation Rates of the $B\ {}^3\Pi_{0^+u}$ State of I_2

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(Received 26 June 1969)

A comparison of the purely radiative decay rates of vibrational levels of the $B\ {}^3\Pi_{0^+u}$ state of I_2 with total decay rates obtained from several independent lifetime measurements has indicated a significant amount of spontaneous predissociation of the B state. We present here a calculation of the observed relative predissociation rates by means of a model consisting of a repulsive 1_u state which is coupled to the $v'J'$ levels of the B state by rotational and electronic angular-momentum terms neglected in the zeroth-order Hamiltonian. The heterogeneous predissociation rate between a bound $v'J'$ level and a continuum level at the same energy is calculated from Kronig's theory using exact wavefunctions for both levels. The dependence of this rate on the rotational level J' is taken into account, together with the fractional population of the $v'J'$ levels which were excited in the measurement of the total decay rates. Excellent agreement is found between the calculated and observed relative predissociation rates at regions about v' of 14, 25, and 50 of the B state for one position of the repulsive state lying very near the repulsive wall of the B state over the energy range 17 300–20 000 cm^{-1}. The position of this state relative to the $B\ {}^3\Pi_{0^+u}$ and $A\ {}^3\Pi_{1u}$ states agrees well with Mulliken's prediction of the location of the ${}^1\Pi_{1u}$ state of I_2.

INTRODUCTION

Recent studies of the I_2 molecule have centered about several properties that can be related to the effects of repulsive electronic states which arise from the lowest ${}^2P_{3/2}+{}^2P_{3/2}$ iodine atom configuration. In the experiments of Wasserman, Falconer, and Yager,[1] Busch,

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[1] E. Wasserman, W. E. Falconer, and W. A. Yager, J. Chem. Phys. **49**, 1971 (1968). This work is reported in more detail in Ber. Bunsenges. Physik. Chem. **72**, 248 (1968).

Mahoney, Morse, and Wilson,[2] and Brewer and Tellinghuisen,[3] ${}^2P_{3/2}$ atoms have been seen as a result of excitation into the banded region of the B state. Other measurements of the magnetic-field quenching of the B–X fluorescence by Degenkolb, Steinfeld, Wasserman, and Klemperer,[4] and line-strength measurements by Chutjian and James[5] have shown the presence of a number of processes producing two ${}^2P_{3/2}$ iodine atoms, and have given quantitative measurements of their rates. Degenkolb *et al.* were also able to trace out a portion of the repulsive 0^-_u state responsible for the magnetically induced quenching.

In the present work we explore the predissociative property of the B state a bit further. By assuming a repulsive state of the form r^{-12} (correlating to ground-state iodine atoms), we were able to obtain very good agreement with the observed predissociation rates[5] of vibrational regions of the B state whose lifetimes had been measured with atomic-line excitations by two independent techniques.[6,7] The calculated relative rates were quite sensitive to the position of the repulsive state, and good agreement was found at one unique position of the state. This position agrees very closely with that predicted by Mulliken for the ${}^1\Pi_{1u}$ state, and it is this state which is causing the spontaneous predissociation of the B state.

THEORETICAL CONSIDERATIONS

Following the treatment of Wentzel[8] and Kronig,[9] we can write the nonradiative predissociation rate A_{nr} as

$$A_{nr}(\text{sec}^{-1}) = (2\pi/\hbar)\,|\langle \Omega_c E_c J\,|\,\mathbf{H}'\,|\,\Omega_b v J\rangle|^2, \quad (1)$$

where the subscripts b and c denote bound and continuum states, respectively. Here, $2\pi\hbar$ is Planck's constant, and the quantity in the brackets is the matrix element connecting the bound electronic, vibrational, rotational level, having quantum numbers Ω_b, v, and J, with the continuum state at the same energy E_c as the bound state, and having an electronic angular momentum Ω_c and a rotational barrier $J(J+1)/r^2$, where r is the internuclear separation. The operator $\mathbf{H}'$ is that part of the total Hamiltonian operator for the nuclei and electrons which was neglected in the zeroth-order approximations $\langle \Omega_c E_c J\,|$ and $|\,\Omega_b v J\rangle$. The detailed form of $\mathbf{H}'$ is given by Kronig for homogeneous ($\Omega_c - \Omega_b = \Delta\Omega = 0$) and heterogeneous ($\Delta\Omega = \pm 1$) predissociations. In the case of I_2 we may only have a heterogeneous predissociation ($1_u \leftarrow 0^+_u$, $\Delta\Omega = +1$) to either or both the nearby $A\,{}^3\Pi_{1u}$ and ${}^1\Pi_{1u}$ states, and $\mathbf{H}'$ in this case is the product of a rotational B value $(\hbar^2 N_0/2\mu) r^{-2}$, (here, μ is the reduced mass of I_2 in Astons and N_0 is Avogadro's number), and certain electronic and nuclear angular-momentum operators. The electronic operators are of the form

$$\sum_i [\xi_i(\partial/\partial\eta_i) - \eta_i(\partial/\partial\xi_i)],$$

where the sum is taken over the coordinates (referred to the molecular frame) of the i electrons of the system, and where two further sums arise by a cyclic variation in the coordinates $\xi\eta\zeta$. These terms give rise to the electronic coupling between 1_u and 0^+_u states, and the explicit form of the electronic contribution $R_e(r)$ to the predissociation will be these angular-momentum operators averaged over the zeroth-order electronic wavefunctions. The nuclear-rotation operator is of the form $\partial/\partial\theta$, where θ is the angle between the internuclear axis and a space-fixed z axis, which has nonzero matrix elements for $\Delta\Omega = \pm 1$ given by[9] $[(J \pm \Omega_b + 1)(J \mp \Omega_b)]^{1/2}$.

The total overlap between the two electronic states will then be the product of a vibrational overlap $\langle E_c J\,|\,r^{-2}\,|\,vJ\rangle$ (whose squared magnitude is analogous to the Franck–Condon factor in bound–bound dipole transitions), the nuclear-rotation matrix element given above, and the electronic overlap $R_e(r)$, whose value can depend on the position of the nuclei, but which we will assume to be a constant R_e in our treatment. Equation (1) then takes the form

$$A_{nr} = (2\pi/\hbar)(\hbar^3 N_0^2/8\pi\mu^2 c)(J \pm \Omega_b + 1)(J \mp \Omega_b) \times |R_e|^2\,|\langle E_c J\,|\,r^{-2}\,|\,vJ\rangle|^2, \quad (2)$$

where c is the speed of light and where the normalization of the last factor is per unit energy (cm^{-1}) range.

In a particular experimental measurement where several v, J levels may contribute to the predissociation, Eq. (2) must be summed over these levels, each weighted by the fraction f_{vJ} of the population in that level. Equation (2) then takes the final form for predissociation of a region of several v's and J's:

$$A_{nr} = (\hbar^2 N_0^2/4\mu^2 c)\,|R_e|^2 \sum_{v,J\ \text{region}} f_{vJ} J(J+1) \times |\langle E_c J\,|\,r^{-2}\,|\,vJ\rangle|^2, \quad (3)$$

where

$$\sum_{v,J\ \text{region}} f_{vJ} = 1,$$

and where we have set Ω_b to zero for the B state of I_2. Using the values $\hbar = 1.05450 \times 10^{-27}$ erg·sec, $N_0 = 6.02252 \times 10^{23}$ mole^{-1}, $c = 2.997925 \times 10^{10}$ cm/sec, and $\mu = 63.4522$ g/mole, we get that $\hbar^2 N_0^2/4\mu^2 c = 0.835363 \times 10^{11}$ sec^{-1}·cm^{-1} Å^4.

We obtain A_{nr} experimentally by taking the difference between the total and radiative rate of depopulation of several vibrational regions of the B state for which the total rate of depopulation was measured. These regions consist of rotational levels in $v = 14, 15, 16$ excited by the sodium D lines (λ5889, 5895 Å), levels in $v = 25, 26, 28$ excited by the mercury green line (λ 5461

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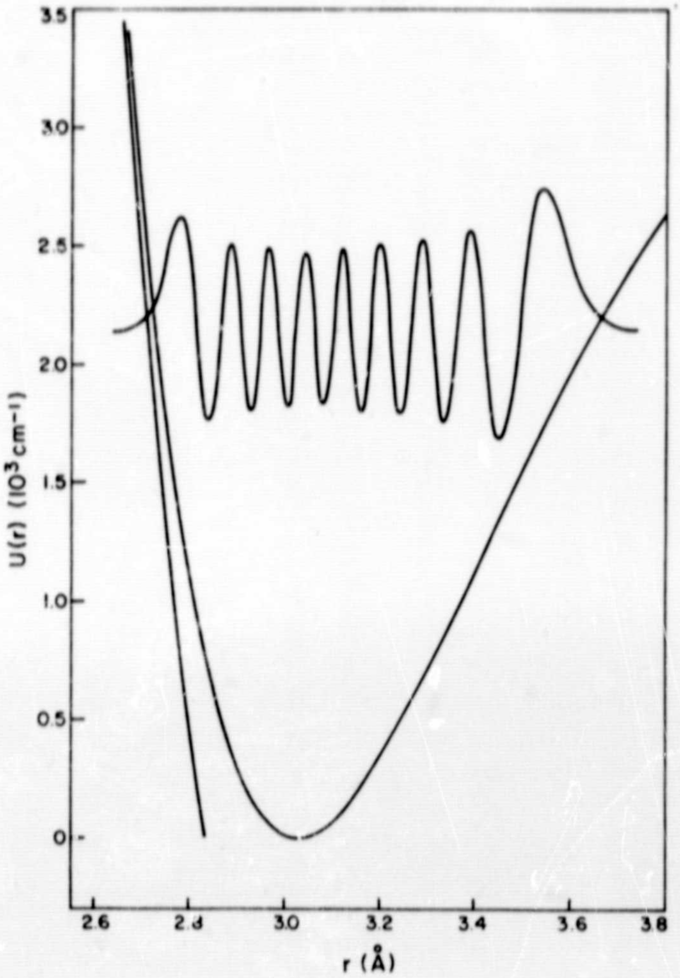

FIG. 1. Wavefunction of the level $v=16$, $J=106$ in the B state of I_2 calculated by the Rydberg–Klein–Rees procedure. The repulsive state is shown crossing the zero of energy at 2.835 Å.

Å), and levels in $v=50$, 51, 53 excited by the cadmium blue line (λ 5086 Å). All quantities on the *right* side of Eq. (3) are known or can be calculated, except $|R_e|^2$, so that one of our three pieces of information can be used to calculate a value for $|R_e|^2$, and all three will be used to determine the position of the one-parameter repulsive state causing the predissociation.

CALCULATION OF THE BOUND AND CONTINUUM WAVEFUNCTIONS

The bound-continuum vibrational overlap in Eq. (3) was evaluated by calculating the wavefunctions of the bound state $|vJ\rangle$ by the Ryberg–Klein–Rees procedure.[10] Briefly, the method here is to calculate a set of classical turning points of the B state for the rotationless ($J=0$) state from spectroscopically determined energy levels. A $J(J+1)/r^2$ barrier is then added to this potential, and the new effective potential is used to solve Schrödinger's equation for a given vibration–rotation level. The wavefunction for the level $v=16$, $J=106$ derived in this way is shown in Fig. 1.

The wavefunction of the continuum state $\langle E_cJ|$ was a one-dimensional, box (energy)-normalized solution to Schrödinger's equation for a potential of the form

$$V(r)\,(\mathrm{cm}^{-1})=(\sigma/r^{12})+[J(J+1)/r^2]\times(\hbar N_0/4\pi c\mu)-3209.9, \quad (4)$$

where σ is the variable position parameter, r is in Ångstrom units, and where the final constant is the energy of the $^2P_{3/2}+{}^2P_{3/2}$ atomic state relative to the zero of energy at the minimum of the B state. To carry out the integration with this potential we used the summed form of the Numerov method.[11] Here, Schrödinger's equation is written in the form $d^2\xi(r)/dr^2=A\xi(r)$, where r is in Bohr radii (a_0) and A is $V(r)-E_c$ divided by the unit of energy $(\hbar N_0/4\pi c a_0^2\mu)=0.948772$ cm^{-1}. The reduced solution $\xi(r)$ at each point r is related to the continuum solution $\psi(r)$ by

$$\psi(r)=\xi(r)/[1-(b^2A/12)],$$

where b is the step size.

The computation of $\psi(r)$ was carried out to a distance of 12 a_0 by which time the wavelength and peak amplitude had reached a constant value. The normalization was carried out to a large value of $r=r_\infty$ of $\sim 8\times10^5$ a_0 and $\psi(r)$ normalized so that

$$\int_0^{r_\infty}\psi(r)^2dr=1.$$

The corresponding energy spacing ϵ (in cm^{-1}) of the states in the "continuum" is given by $\epsilon=6.12013E_c$ (cm^{-1})$^{1/2}/r_\infty$(a_0) and was approximately 5×10^{-4} cm^{-1}. The final energy-normalized wavefunction was then $\langle E_cJ|=\epsilon^{-1/2}\psi(r)$ which now has units of (cm^{-1})$^{-1/2}$. This function is plotted in Fig. 2 for one position of the repulsive state and at the same energy E_c of the $v=16$, $J=106$ level of Fig. 1.

The step size used in the above calculations was 0.002 Å, and was slightly smaller than 0.0025 Å used in a comparable calculation by Zare.[10] This gave a sampling of about 20 points per node-to-node distance for the bound states and about 15 points for the continuum states.

COMPARISON OF CALCULATED AND OBSERVED PREDISSOCIATION RATES

In the next-to-last column of Table II we present the measured nonradiative rates at regions about $v=14$, 25, and 50. These are the differences between the total and radiative decay rates of Refs. (5)–(7) and are individually displayed in Table III of Ref. 5 for $v=14$ and 25. The radiative decay rate of levels in the region of $v=50$ was not measured (and would be extremely difficult to measure since the blending at such high v is even greater than at $v=25$), but was extrapolated from the measurements of Ref. 5. The extrapolation

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takes into account the calculated linear variation of the mean cubed wavenumber of the B–X emission with v, and assumes that the electronic contribution to the transition moment in the radiation process will be constant to within about 20%.[12]

TABLE I. Transitions, fractional populations of the levels v, J, and weighted rotational dependences used to calculate predissociative rates from Eq. (3). The transitions in braces are those which were combined into the single J and f_{vJ} shown.

Transition		f_{vJ}	$f_{vJ}J(J+1)$
14–1 $P(107)$	$J=109$	0.288	3453
14–1 $P(114)$			
15–2 $R(43)$	$J=41$	0.563	969.5
15–2 $P(38)$			
16–2 $R(105)$		0.149	1690
25–0 $R(33)$		0.494	587.9
26–0 $R(85)$		0.432	3232
28–1 $R(50)$		0.074	196.2
50–0 $R(31)$	$J=31$	0.493	489.0
50–0 $P(30)$			
51–0 $P(45)$		0.322	637.6
53–0 $R(64)$		0.185	793.7

The v, J levels to which absorption takes place when I_2 is excited by atomic lines are known partly through experimental observations and can be calculated quite accurately from spectroscopic constants of the B[13] and X[14] states. Brown and Klemperer,[15] Steinfeld and Klemperer,[16] and Steinfeld *et al.*[13] have observed several transitions excited by the sodium D, mercury green, and cadmium blue lines, and the results of their observations are included in the first column of Table I. In addition to the observed lines, several more calculated lines were included in Table I which fell within 0.3 cm^{-1} of the mercury green line. The additional lines 28–1 $R(50)$ and 26–0 $R(85)$ are two such lines which would get excited by a broadened green line. These transitions are also noted by Pringsheim.[17]

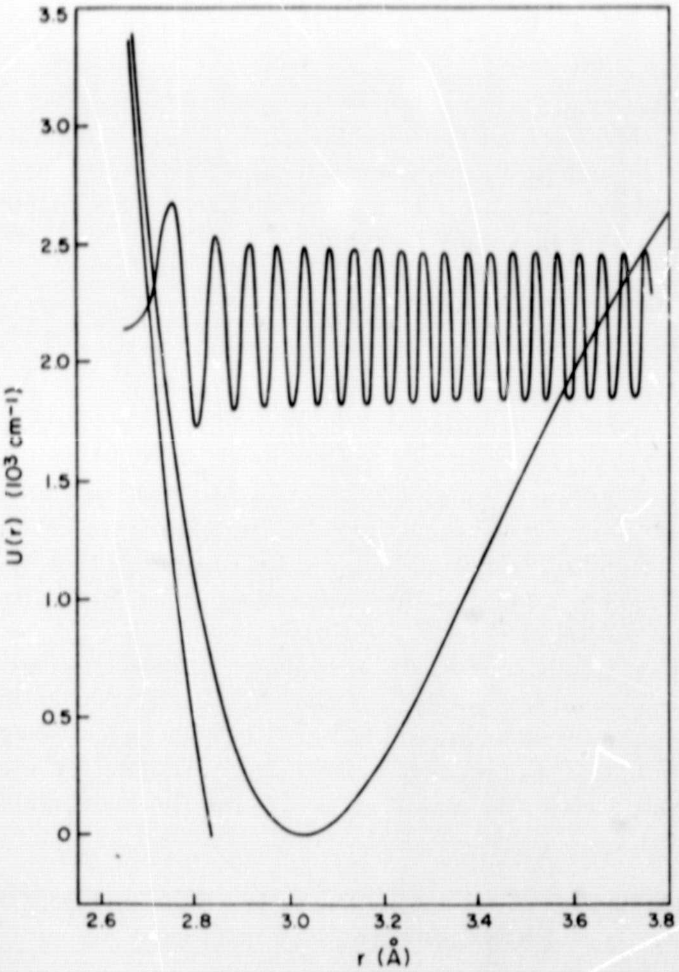

FIG. 2. Wavefunction of the continuum level at the same energy as the bound level in Fig. 1.

The fraction f_{vJ} of absorption to the level v, J was calculated for each line in the three regions by first calculating the quantity $N_{v''J''}q_{vv''}$, which is proportional to the excited-state population. Here $N_{v''J''}$ is the ground-state population of the level v'', J'' (where $J''=J\pm1$) derived from the I_2 partition function, and $q_{vv''}$ the Franck–Condon factor for the transition. The fraction f_{vJ} is the ratio of the population in the upper v, J level to the population of all levels in the region, or

$$f_{vJ}=N_{v''J\pm1}q_{vv''}\Big/\sum_{v,J\ \text{region}} N_{v''J\pm1}q_{vv''}.$$

In order to reduce the number of overlap computations involved, several rotational transitions having neighboring J's in the same vibrational band were combined into a single transition having the square root of the average value of $J(J+1)$ and the sum of the individual f_{vJ}. These combined transitions were 14–1 $P(114)$ and $P(107)$, 15–2 $R(43)$ and $P(38)$, and 50–0 $P(30)$ and $R(31)$. The last column in Table I gives the properly weighted v, J dependence of the transition rate in Eq. (3).

RESULTS AND DISCUSSION

The position of the repulsive state of Eq. (4) was varied from 2.5 to 3.0 Å in steps of 0.05 Å. (The distances r given are those which determine, for $J=0$ in Eq. (4), the parameter σ equal to $3209.9r^{12}$.) The best fit to the experimental rates over the energy range

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[12] The radiative rate was then $3.19\times10^6\ sec^{-1}$, or approximately two times *larger* than the total rate of Ref. 6 for excitation with the Cd line. A careful remeasurement of this lifetime by P. T. Cunningham (University California Radiation Laboratory Rept. No. 18419, 1968) with better signal to noise gave a total rate of $6.58\times10^6\ sec^{-1}$, which was used in this work.

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TABLE II. Values of the vibrational overlap $\langle E_0J | r^{-2} | vJ \rangle$ for each transition studied, together with the calculated and experimental predissociation rates. The last column gives the calculated A_{nr} using the value of $|R_e|^2 = 0.00258$. The repulsive curve is at 2.835 Å (σ equal to 8.651×10^8).

Level (v, J)	$\langle E_0J \| r^{-2} \| vJ \rangle$ (cm$^{1/2}$ Å^{-2}) (10^{-4})	Relative rates		Absolute rates (10^6 sec^{-1})	
		Measured	Calculated	Measured	Calculated
(14,109)	4.063	1.00	1.00	2.76	2.76
(15,41)	−5.208				
(16,106)	5.154				
(25,34)	−10.70	3.44	3.47	9.50	9.58
(26,86)	10.43				
(28,51)	11.56				
(50,31)	9.271	1.23	1.15	3.39	3.18
(51,44)	−8.966				
(53,65)	−8.266				

17 300–20 000 cm^{-1} occurred at a distance of 2.835 Å, or $\sigma = 8.651 \times 10^8$. (This position is also the one drawn in Figs. 1 and 2.) The results of this fit are shown in Table II, and also in Fig. 3, where the relative rates for positions 0.002 Å to the right and left of 2.835 Å are also shown.

The results at other positions of the repulsive state can be explained qualitatively in terms of the distance between the left-hand turning points of the bound and continuum wavefunctions (see, for example, Figs. 1 and 2). As we proceed to the right (larger r) of 2.835 Å, the bound-state turning points at $v \sim 14$ and 25 approach their respective continuum-state turning points, (the overlap increases), while the bound and continuum wavefunctions at $v \sim 50$ pass through their maxima and recede. The relative predissociation rates at 2.90 Å (where the repulsive state has already crossed into the B state) then become 1.00:2.71:0.11 for the regions 14:25:50, corresponding to the passage of the continuum turning points at $v \sim 50$ away from the left-hand turning points of the B state. For distances to the left (smaller r) of 2.835 Å, the distance between the bound and continuum turning points for $v \sim 14$ and 25 is greater than at $v \sim 50$, and the relative rates are, for example, 1.00:0.31:10.9 at 2.55 Å.

We should mention at this point that although this qualitative picture is helpful, it is not quite correct to say that all the overlap occurs at the left-hand turning points. This is assumed in the delta-function approximation (i.e., a delta function in distance) to the continuum states. In our calculations at $v = 14$, 15, 16, for example, we found that the overlap at a point just after the left-hand turning point of the bound state was within a factor of 2 of its final value, indicating that considerable enhancement or cancellation occurs at the right-hand turning point. (This was to be expected for I_2 since the "wavelengths" of the bound and continuum states were within 60% of one another.) We also found that this deviation from the final value was not constant for $v \sim 14$ and 50, so that some error will occur in the *relative* values of the overlaps of these levels. Thus, we feel that numerical solutions to Schrödinger's equation will be more accurate than the delta-function approximation for cases where the kinetic energies of the overlapping states are close to one another (say, to within a factor of 10, or wavelengths within a factor of 3).

The actual values of the overlaps and the calculated and measured predissociation rates are collected in Table II. The errors in the measured rates are about ±15% of the values shown. By comparing the measured A_{nr} and the calculated overlaps in the first region ($v \sim 14$) we were able to calculate a value of the electronic overlap of the 1_u and $0^+{}_u$ states of $|R_e|^2 = 0.00258$. This value of $|R_e|^2$ was then used to calculate the absolute rates in the second and third regions.[18] (We should note that since this value of $|R_e|^2$ is a scaling factor which brings the calculated rates into agreement with the measured A_{nr}, its value is not needed for the calculation of the *relative* predissociation rates. The problem is then still the determination of the single parameter σ.)

There is some question as to whether our calculated state is the $A\ {}^3\Pi_{1u}$ or ${}^1\Pi_{1u}$ state of I_2. Absorption to the ${}^3\Pi_{1u}$ state has been seen by Brown[19] and Ham,[20] and the absorption was found to have a maximum at 14 900 cm^{-1}.[20] Mulliken[21,22] has given the separation of the two states at the r_e'' of the X state (using his Interpretation I with the ${}^1\Pi$ at 19 470 cm^{-1}, and after taking into account the depressing effects of higher perturbing ${}^3\Sigma_u{}^+$ and ${}^3\Delta_{1u}$ states on the calculated ${}^1\Pi$–${}^3\Pi$ separation) to

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[18] An accurate theoretical estimate of this quantity is difficult to come by. From sum-rule considerations of transitions to *all* electronic states of the manifold, it can have at most a value of the order of unity. Van Vleck [J. Chem. Phys. **4**, 327 (1936)] has calculated for a homogeneous transition the average of the square of the electronic angular momenta about the molecular-fixed ξ and η axes for H_2, and obtains a value of 0.394. The point here is that other positions of the repulsive state in our calculations at which a good fit to the relative predissociation rates might accidentally occur give a value of $|R_e|^2$ of the order of 10^2 or greater. This comes about at distances less than 2.80 Å, where the vibrational overlap is very small, and where $|R_e|^2$ has to increase to values much greater than unity to give the experimental A_{nr}. The position of the curve at 2.835 Å thus gives a good fit to the relative rates, and provides as well a reasonable value of $|R_e|^2$.

[19] W. G. Brown, Phys. Rev. **38**, 1187 (1931).

[20] J. S. Ham, J. Am. Chem. Soc. **76**, 3886 (1954).

[21] R. S. Mulliken, Phys. Rev. **57**, 500 (1940).

[22] R. S. Mulliken (private communication).

be ~4570 cm^{-1}. At r_e'' of 2.665 Å, the energy of our calculated state is 19 300 cm^{-1}, so that the $^1\Pi$–$^3\Pi$ separation is 4400 cm^{-1}, which is close to Mulliken's prediction. The position of the $^1\Pi$ relative to the B state is estimated to be 270 cm^{-1} *above* the B state,[22] but is thought to run below the B state since no breaking-off of emission due to the predissociation has been observed. The calculated position of our repulsive state at r_e'' is 50 cm^{-1} above the B state, and quickly falls to 2000 cm^{-1} below the B state at 2.75 Å.

This last result, however, does not imply that the two states actually cross near r_e''. If the repulsive curve were at 2.832 Å, the relative rates would be 1.00:3.93: 1.40, which is still within the experimental error of the observed rates in Table II. The repulsive state in this case would be 30 cm^{-1} below the B state at r_e''. We should emphasize that the potential energy of these states at $r \sim r_e''$ is changing at the rate of 40 cm^{-1}/0.001 Å, so that the 50-cm^{-1} separation is also less than the combined error in the calculation of the turning points, and more importantly, in the assumption of a one-parameter r^{-12} potential. In regard to this last point, we know that at distances less than r_e'', where the multiplet splitting is less than the singlet–triplet separation, the $^1\Pi$ must eventually lie above the $^3\Pi_{0^+u}$ state, so that an eventual crossing of the two states must occur.[21] The repulsive state of our calculation does not yet rise more rapidly than the B state at D_e', so that the exact point of crossing is difficult to estimate from our calculation, although it probably occurs above the dissociation limit of the B state.

The position of our calculated repulsive state seems to be consistent with a depressed $^1\Pi_{1u}$ lying close enough to the B state to cause some predissociation. Another piece of evidence helpful in the assignment lies in the expected[21] and observed[5] background absorption in the vicinity of the B state. Mulliken states that the $^1\Pi \leftarrow X$ absorption should be a weak one buried under the strong continuum and bands of the $B \leftarrow X$ absorption. We can get a rough estimate of the intensity of the $^1\Pi \leftarrow X$ absorption from the continuum and banded absorption measurements of Ref. 5. We calculate that the average continuum absorption is 20%±10% of the banded absorption at the two wavelengths (6016 and 5460 Å) at which the continuum absorption was measured.[5] The calculation was done at each wavelength by comparing the total line strength of 50 rotational lines in a 10–12 cm^{-1} frequency interval about each wavelength with the continuum absorption over the same interval. From this continuum/banded ratio we can crudely calculate the product[21] electronic degeneracy (G')×dipole strength (D) of the $^1\Pi \leftarrow X$ to be 20%±10% of $G'D$ for $B \leftarrow X$, or $G'D\ (^1\Pi \leftarrow X) = (116 \pm 58) \times 10^{-4}$ Å^2. This is in rough agreement with Mulliken's estimate[22] of 67.2×10^{-4} Å^2, again using his Interpretation I. Although one could argue that this observed background could also be absorption into the A-state continuum, we would expect this type of absorption to be even weaker than the weak maximum A state absorption at 14 900 cm^{-1}. It seems more likely that most of the background absorption is occurring into the turning-point regions of the $^1\Pi$ state.

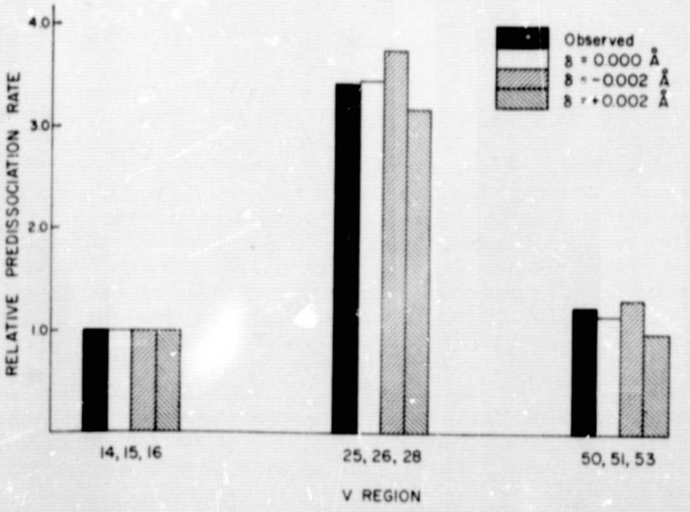

FIG. 3. Variation of the relative predissociation rates with position of the r^{-12} repulsive state. The quantity δ is the deviation from the best-fit position of 2.835 Å.

We can also explore the possibility of whether the A state in its known position could be causing the predissociation of the B state. A calculation of the relative predissociation rates with a Lennard-Jones 6–12 potential (with a well depth of 645 cm^{-1} and a crossing radius of 2.90 Å) gave a relative rate of 1.00:0.62:52.7 and a value of $|R_e|^2$ of 6 × 10^4. From these pieces of information[18] it seems almost certain that the state we have calculated is the $^1\Pi_{1u}$ state of I_2. The position and assignment of this state also explain the continuum absorption underlying the bands in the $B \leftarrow X$ system.

CONCLUSIONS

Good agreement was found between measured and calculated relative predissociation rates of three vibrational regions of the B state of I_2. The calculation assumed a repulsive r^{-12} potential for the 1_u state causing the predissociation. Both the $J(J+1)$ dependence of the heterogeneous rate as well as the relative populations of the predissociating v, J levels in each region were taken into account.

From its position relative to the $A\ ^3\Pi_{1u}$ and $B\ ^3\Pi_{0^+u}$ states, this calculated state is almost certainly the $^1\Pi_{1u}$ state of I_2. The presence of this state very close to the B state is consistent with the observed predissociation of the B state, and is almost certainly responsible for the observed continuum absorption underlying the B state.

ACKNOWLEDGMENTS

We are very grateful to Professor T. C. James and Professor G. A. Segal for helpful discussions and comments, and to Professor R. S. Mulliken for several helpful correspondences. Support for this work by the National Science Foundation (GP-5294) and the National Aeronautics and Space Administration (NGR-05-018-065) is also gratefully acknowledged.