Iodine Revisited ⊘

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(1) Previous estimates of the vertical energies of the valence-shell states of the iodine molecule are revised in the light of newer information. Correspondingly, a complete set of estimated potential curves is drawn for those valence-shell states which dissociate into ground-configuration atoms. In the light of this set of curves, conclusions in several recent papers are reviewed and in some cases revised. LeRoy's 0_g^+ excited state is reconsidered. Predissociations of the 2431, $^3\Pi_{0^+u}(B)$ state are discussed. It is definitely concluded that the state mainly responsible for magnetic predissociation is the corresponding $^3\Pi_{0^-u}$ state and *not* a $^3\Sigma_u^+(0^-)$ state. It is, however, possible that a $^3\Sigma_u^+(0^-)$ state, probably that of the 1441 configuration, makes some contribution to the magnetic predissociation near $v=10$. Spontaneous predissociation and collision-induced predissociation are also discussed. (2) Previous calculations for the estimation of the wavefunctions, relative energies, and transition probabilities from the normal state 2440, $^1\Sigma_g^+(X)$, of the several states of the 2431 configuration, are revised in the light of newer evidence. It is concluded that of the fairly strong visible absorption, perhaps 20% is due to the transition $^1\Pi_u \leftarrow X$, the rest being $^3\Pi_{0^+u} \leftarrow X$ and a little $^3\Pi_{1u} \leftarrow X$. It is concluded that the $^3\Pi_{0^+u} \leftarrow X$ transition moment results largely from case c mixing of 2341, $^3\Pi_{0^+g}$ into X and relatively little directly from the mixing of 1441, $^1\Sigma_u^+$ into $^3\Pi_{0^+u}$, but that a cross term arising from the joint effect of these two admixtures is also important. (3) Contrary to some writers, the conclusion that the intense uv room temperature absorption bands peaking at about 1825 Å (part of the Cordes bands) belong to the transition 1441, $^1\Sigma_u^+ \leftarrow X (D \leftarrow X)$ of the VN type, is strongly reaffirmed. The corresponding 1441, $^3\Sigma_u^+(1_u)$ transition is identified with the weak I_2 continuous absorption peaking near 2700 Å. Possible minor overlapping contributions from other weakly allowed transitions are discussed. The extension of the $D \leftarrow X$ bands to longer wavelengths in high-temperature absorption is reviewed. An equation given by Wieland, aside from some uncertainty in the vibrational numbering, accurately describes the vibrational pattern of the D levels. The high-temperature absorption bands with low-frequency edges at λ 3427 and λ 3263 (Skorko bands) are, respectively, attributed to the transitions 1432, $^3\Pi_{2g} \leftarrow 2431$, $^3\Pi_{2u}$ and 1432, $^3\Pi_{1g} \leftarrow 2431$, $^3\Pi_{1u}$ which theoretically should be intrinsically intense like the $D \leftarrow X$ bands. (4) Starting from semiclassical considerations in an accompanying paper on the role of kinetic energy in the Franck–Condon theory, and taking into account various experimental observations, it is concluded that the uv McLennan bands which culminate in a relatively intense series of fluctuations at about λ3250 are a part of the fluorescence spectrum resulting from excitation into vibrational levels of the D state; the resonance series at higher frequencies belongs to the same fluorescence spectrum ("primary fluorescence spectrum"). Other McLennan bands at longer wavelengths are attributed to transitions down to repulsive curves from other initial electronic states produced by collisions ("secondary fluorescence spectrum"). It is shown that the "fluctuation interval" in the λ3250 group has a magnitude, and varies with exciting frequency, in reasonable accord with the theory. From its magnitude approximate conclusions are drawn about the minimum energy and equilibrium internuclear distance for the D state potential curve. Further experimental work should be of interest. (5) The emission band systems obtained in the presence of considerable pressures of foreign gases (N_2 or Ar) are discussed, and reasonable assignments for some of their upper, ion-pair type, initial states are given. In the case of the very strong region with maximum near λ 3425, proposals of Verma, Wieland, and Tellinghuisen are considered, but further work will be necessary before definite conclusions can be reached. Very likely more than one electronic transition may be involved.

I. INTRODUCTION

Quantum theory shows that the iodine molecule must possess a rather large number of valence-shell electronic states, followed, mostly at higher energies, by Rydberg states. "Valence-shell states" means states whose MO (molecular orbital) electron configurations are of the type $\sigma_g^2\sigma_u^2\sigma_g^m\pi_u^p\pi_g^q\sigma_u^n$ with $m+n+p+q=10$ and with MO's σ_g, σ_u of the forms $5s \pm 5s$ and $5p\sigma \pm 5p\sigma$, and π_u, π_g of the forms $5p\pi \pm 5p\pi$, in simplest LCAO approximation. For the ground state of I_2, $m=2$, $p=q=4$, $n=0$, briefly 2440. Hereafter the various electron configurations will be denoted by giving in sequence the values of m, p, q, and n; for example, the lowest excited states belong to the configuration 2431.

A great many papers have been devoted to the correlation of experimental, mostly spectroscopic, evidence with predictions on the potential curves and other features of the valence-shell states. Much valuable evidence and interpretation has accumulated in recent years, especially on the ground state (X) and on the 2431 states, particularly the $^3\Pi_{0^+u}$ state of this configuration, the "B" state. However, the nature of the higher states of I_2 has remained confused and controversial. It now seems worthwhile, aided by certain newer items of empirical evidence, to present a revision of earlier approximate predictions[1] of energy levels, potential curves, and related features, together with conclusions derived therefrom.

One set of approximate predictions (see Table I) concerns the vertical energies of the valence-shell states measured upward from the bottom of the potential curve of state X; in other words, the estimated energies of the various states at an internuclear distance R equal
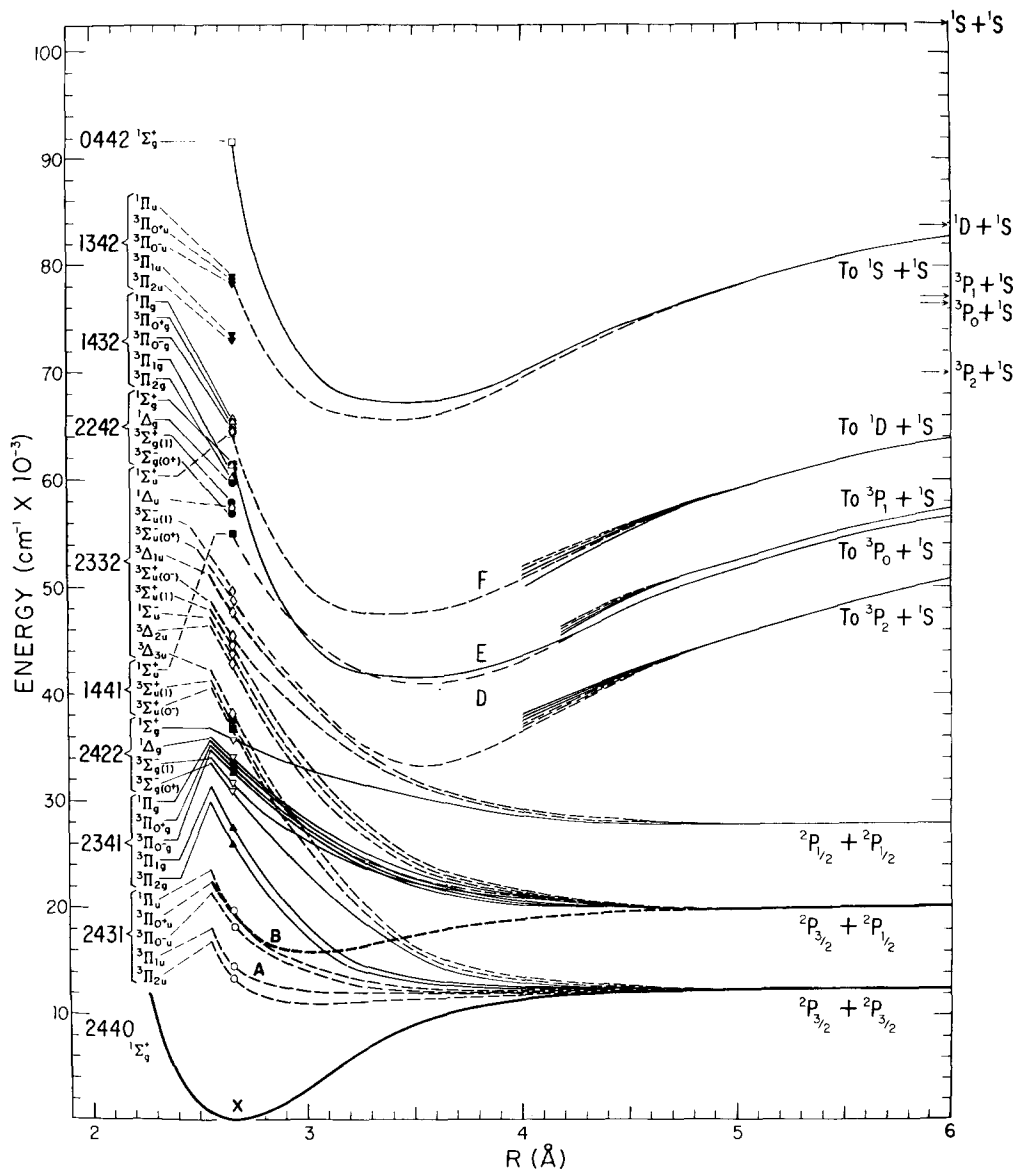
FIG. 1. Estimated potential curves for valence-shell states of iodine (see Secs. II and III). Each curve is drawn to pass through one point at 2.666 Å (R_e of state X) obtained from an estimated vertical energy at that R value (see Table I). The curves for states of even (g) parity are shown by full lines, those for states of odd (u) parity by dashed lines. The asymptote of each of the lower set of curves (those which dissociate to two ground-configuration atoms) is reliably known theoretically, except that in few cases, it is not certain which of two curves of the same case-c type and nearly the same estimated vertical energy is really lower; for example, it is possible that the vertical energies and the dissociation asymptotes of the 2341, $^3\Pi_0{}^+{}_g$ and the 2422, $^3\Sigma_g{}^-$ (0^+) curves should be reversed. Except for the X and B states (shown by heavy curves), and to some extent the A state, the detailed froms of the curves are not known, but they have been drawn in accordance with qualitative considerations on bonding or antibonding characteristics of the MO's involved (see Sec. III). The upper set of states are of ion-pair character, and tend to dissociate to various states of I$^+$ plus$\cdots$ $5p^6$, ^1S of I$^-$ whose energies are indicated at the right of the figure, but actually many of them must shortcut to dissociate to yield one excited-configuration and one ground-configuration atom (see Sec. III). For most of these states, only the vertical energy at R_e of state X, and the estimated forms of the curves at large R (based on a $1/R$ ion-pair potential modified by some allowance for polarization) are shown. Complete curves are sketched in for a few cases; for the E and F states (see Sec. VIII) the energies of the minima of their potential curves, and some indications as to their R_e values, are known. The position shown for the D curve is uncertain, but its approximate location is indicated by evidence discussed in Secs. VII and VIII.

to the equilibrium distance R_e (namely 2.666 Å) of state X.[2] Combining these vertical energies with other theoretical considerations on shapes and asymptotes permits the sketching in of potential curves for the various states (see Fig. 1). While the curves shown cannot possibly be quantitatively correct, they should be useful as forming a sort of zeroth approximation to the true curves. However, the curves of the X and B states[3] are rather accurately known from experimental data.

TABLE I. Estimated vertical energies, predicted dissociation products, and major predicted transitions, for valence-shell electronic states of I_2. Observed quantities are noted in a few cases. For the states called E and F, observed T_0 but not vertical energies are available. It is not certain that E is 1432, $^3\Pi_0^+{}_g$; it may be 2242, $^1\Sigma_g^+$, in which case the upper state of the λ 3425 bands is 1432, $^3\Pi_0^+{}_g$ (see Sec. VIII).

Under "Predicted Dissociation Products," aa means dissociation to $^2P_{3/2}+^2P_{3/2}$ atoms, ab to $^2P_{3/2}+^2P_{1/2}$, and bb to $^2P_{1/2}+^2P_{1/2}$; the correctness of these predictions is unquestionable except in cases where the predicted vertical energies of states of equal case c type are not in correct order—for example, if the 2341, $^3\Pi_0^+{}_g$ state is above instead of below the $^3\Sigma_g^-(0_g^+)$ state, the dissociation product correlations aa and ab (indicated by asterisks in the table) must be reversed. The higher-energy valence-shell states have ion-pair structure and *tend* to dissociate into $I^-(^1S)$ plus $I^+(^3P_2$ or $^3P_1$ or $^3P_0$ or ^1D or $^1S)$, but actually must shortcut in many or most cases into one $^2P_{3/2}$ or $^2P_{1/2}$ ground-configuration atom and one excited atom (see last paragraph of Sec. III); under "Predicted Dissociation Products" the I^+ state into which dissociation tends to occur according to case-c rules is listed, followed in some cases in parentheses by an alternative into which dissociation would tend to occur if there were conservation of spin multiplicity (see Sec. III).

Under "Major predicted transitions," f, s, m, w, and v, respectively mean forbidden, strong, medium, weak, and very. Under "Absorption from X" several observed cases are listed. Under "Emission," predictions for the ion-pair states are for *groups* of states belonging to the listed configuration; in each case the predicted transitions (except for relatively weak $\Delta\Omega=1$ transitions) are subject to the rule $\Delta\Omega=0$; for example, for the transitions from the 1342 to the 2341 configuration, only $^1\Pi_u\rightarrow^1\Pi_g$, $^3\Pi_0^+{}_u\rightarrow^3\Pi_0^+{}_g$, $^3\Pi_0^-{}_u\rightarrow^3\Pi_0^-{}_g$, $^3\Pi_{1u}\rightarrow^3\Pi_{1g}$, $^3\Pi_{2u}\rightarrow^3\Pi_{2g}$, and (weaker) $^1\Pi_u\rightarrow^3\Pi_{1g}$ and $^3\Pi_{1u}\rightarrow^1\Pi_g$ can occur strongly. Additional, mostly vvw, transitions from the ion-pair states are not listed. However, one such transition, $F\rightarrow X$, identified as most probably 2332, $^1\Sigma_u^+\rightarrow X$, is observed with very appreciable intensity; this is explainable by intensity stealing by $F\rightarrow X$ from $D\rightarrow X$. Transitions $E\rightarrow B$ and the λ 3425 bands (see Sec. VIII) are also observed with considerable or high intensity when inert gases are added to I_2.

Estimated mean vertical energy (eV)	Electron configuration	Electronic state		Estimated vertical energy (eV)	Predicted dissociation products	Major predicted transitions	
						Absorption from X	Emission
11.3	0442	$^1\Sigma_g^+$	0^+	11.3	^1S	f	
		$^1\Pi_u$	1	9.8	^1D	vw	
9.4	1342	$^3\Pi_u$	0^+	9.8	$^1S(^3P_0)$	m	s to 2341
			0^-	9.8	$^3P_1$	f	s to 1432
			1	9.1	$^3P_1$	vvw	w to 2242
			2	8.9	$^1D(^3P_2)$	f	
		$^1\Pi_g$	1	8.1	^1D		s to 2431
		$^3\Pi_g$	$0^+(E?)$	8.1; T_0 obs	$^1D(^3P_0)$		w to 1441
7.8	1432		0^-	8.0	$^3P_1$	f	w to 2332
			1	7.5	$^3P_1$		
			2	7.4	$^3P_2$		
		$^1\Sigma_g^+$	$0^+(E??)$	7.6	$^3P_0(^1D)$		
7.4	2242	$^1\Delta_g$	2	7.4	^1D	f	s to 2332
		$^3\Sigma_g^-$	1	7.1	$^3P_2$		
			0^+	7.0	$^3P_2$		
		$^1\Sigma_u^+$	$0^+(F)$	8.0; T_0 obs	^1D	m	s to 2422
		$^1\Delta_u$	2	7.1	$^3P_2(^1D)$	f	w to 2341
		$^3\Sigma_u^-$	1	6.1	$^3P_2$	vw	
			0^+	6.0	$^3P_2$	w	
5.8	2332	$^3\Sigma_u^+$	0^-	5.6	bb	f	
			1	5.5	ab	vw	
		$^1\Sigma_u^-$	0^-	5.4	ab	f	...
		$^3\Delta_u$	1	5.9	bb	vw	
			2	5.3	ab	f	
			3	4.7	aa	f	
		$^1\Sigma_u^+$	$0^+(D)$	6.77 obs	$^3P_0(^1D)$	vs obs	vs obs
5.7	1441	$^3\Sigma_u^+$	1	4.57 obs	ab	vvw obs	...
			0^-	4.5	aa	f	...

TABLE I (*Continued*)

Estimated mean vertical energy (eV)	Electron configuration	Electronic state		Estimated vertical energy (eV)	Predicted dissociation products	Major predicted transitions	
						Absorption from X	Emission
4.2	2422	$^1\Sigma_g^+$	0^+	4.4	*bb*	f	...
		$^1\Delta_g$	2	4.2	*ab*		
		$^3\Sigma_g^-$	0^+	3.9	*aa**		
			1	3.8	*ab*		
3.7	2341	$^1\Pi_g$	1	4.1	*ab*	f	...
		$^3\Pi_g$	0^+	4.1	*ab**		
			0^-	4.1	*ab*		
			1	3.4	*aa*		
			2	3.2	*aa*		
2.1 obs	2431	$^1\Pi_u$	1	2.38	*aa*	w obs	...
		$^3\Pi_u$	$0^+(B)$	2.37 obs	*ab*	m obs	m to X obs
			0^-	2.34	*aa*	f	...
			1(A)	1.79 obs	*aa*	vw obs	vw to X obs
			2	1.66	*aa*	f	f
0.00 obs	2440	$^1\Sigma_g^+$	$0^+(X)$	0.00	*aa*		

II. THE ESTIMATION OF VERTICAL ENERGIES

In the estimation of the vertical energies for Table I and Fig. 1, the procedure was as follows. First, the mean vertical energy was estimated for each MO configuration, in the same way as previously,[1a] but with one change. Namely, it was, and is here, assumed that configuration 2341 is higher in vertical energy than 2431 by an amount equal to the difference in energy of the I_2^+ states 2430, $^2\Pi_g$ and 2340, $^2\Pi_u$. Previously, this difference was estimated as 0.7 eV, but now it is known experimentally to be 1.6 eV.[4] So now in Table I we have as estimated mean vertical energies, 2.1 eV for 2431 (*exptl*) and 2.1+1.6=3.7 eV for 2341. Similarly a difference of 1.6 eV between 1432 and 1342 is assumed. For 2422, the same difference of 2.1 eV from 2431 is assumed as for 2431 from 2440, giving 2×2.1= 4.2 eV. For 1441, the assigned value 5.7 eV is based on experimental spectroscopic evidence (see Sec. VI). To go from 2422 to 2332, and from 2332 to 2242, a difference of 1.6 eV, the same as from 2430 to 2340, was assumed, and so on.

Within the 2431 configuration, the vertical energies were obtained in part ($^3\Pi_1$ and $^3\Pi_{0+}$ states) from experimental data, in part from these and other data and theoretical considerations (see Sec. V). The vertical energies within the 2341, 1432, and 1342 configurations were estimated by assuming the relative positions of the $^3\Pi_2$, $^3\Pi_1$, $^3\Pi_0^-$, $^3\Pi_0^+$, and $^1\Pi$ states to be approximately the same as in the 2431 configuration; while this procedure is surely not exactly correct, it should not be very badly wrong. Within the configurations 2422 and 2242, the energies of the $^1\Sigma_g^+$, $^1\Delta_g$, and $^3\Sigma_g^-$ states were assumed to be spaced in a manner parallel to those of

the 2420 states of the O_2 molecule, but with a spacing reduced by a factor 0.37, which is the ratio of the π_g minus π_u ionization potentials in the two molecules (equal in iodine to the 2430–2340 I_2^+ energy difference of 1.63 eV, compared with 4.45 eV for the 2410–2320 difference in O_2^+).

Within the configuration 2332, estimated values are again based on a comparison with O_2, for which the states $^3\Delta_u$, $^1\Sigma_u^-$, $^3\Sigma_u^+$, and $^3\Sigma_u^-$ of the configuration 2330 are known, while the positions of $^1\Delta_u$ and $^1\Sigma_u^+$ can be estimated theoretically. In O_2, the states $^3\Delta$, $^1\Sigma^-$, and $^3\Sigma^+$ are close together and all dissociate to ground-state atoms, while $^3\Sigma_u^-$ is 1.7 eV higher. Using again the factor 0.37, $^3\Sigma_u^-$ of 2332 in I_2 is estimated as 0.6 eV above the mean of the other three. Consideration of spin–orbit coupling shows that the $^3\Delta_u$ should be *inverted* with spacings between the three components about the same as the energy difference (about 0.6 eV) between the components $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ of $^2\Pi_g$ or $^2\Pi_u$ of I_2^+. For the $^1\Delta_u$ and $^1\Sigma_u^+$ states of the 2332 configuration of I_2, we use the fact that Recknagel's theoretical formulas[5] for the spacings of the states of a $\pi\pi$ configuration are also applicable to a $\pi^3\pi^3$ configuration which is present in O_2 and here.[6a,6b]

III. THE POTENTIAL CURVES

The potential curves in Fig. 1 fall into two categories[1a]: (1) those which go on dissociation to neutral atoms in their ground state configuration $\cdots 5s^2 5p^5$, in their states $^2P_{3/2}$ or $^2P_{1/2}$, (2) those which tend to go into ions I^+ plus I^- in their ground state configurations, $\cdots 5s^2 5p^4$ for I^+ with states $^3P_2$, $^3P_1$, $^3P_0$, ^1D, and ^1S, and $\cdots 5s^2 5p^6$, ^1S for I^-.

Let us first consider the states in category (1). Given the vertical energies at R_e of state X, the usual case c group-theoretical rules in terms of inversion character (g or u), Ω values, and, for 0 states, the distinction of 0^+ and 0^- states, and given also the noncrossing rule for states of like symmetry, the qualitative correlation of each state from R_e out to dissociation is fixed.[1a] However, in cases where two states of the same symmetry species are near each other in *estimated* vertical energy, it is not unlikely that the *true* vertical energies may be in reverse order so that the true dissociation correlations would be correspondingly reversed.

Most of the curves of category (1) are essentially repulsion curves, with only very shallow minima at large R values due to London dispersion energies going as R^{-6}, supplemented or opposed by quadrupole–quadrupole energies[8] going as R^{-5} in case one or both atoms are in the $^2P_{3/2}$ state (these latter energies vanish if both are in the $^2P_{1/2}$ state). Only states X and B have fairly deep minima.

If, for the moment, we leave aside the long-range forces, the fall or rise of any curve as R decreases should be related to the numbers and types of bonding and antibonding electrons in its electron configuration. In H_2 the states which at small R are described as $(\sigma_g 1s)^2$, $^1\Sigma_g^+$ and $(\sigma_g 1s)(\sigma_u 1s)$, $^3\Sigma_u^+$ show, respectively, a rapid fall and a roughly equally rapid rise in energy as R decreases from ∞. The corresponding states in I_2, so far as σ electrons are concerned, are 2440, $^1\Sigma_g^+$ and 1441, $^3\Sigma_u^+$. The 2440 state shows an attractive potential curve corresponding to the two σ_g bonding electrons. It is then to be expected that the 1441, $^3\Sigma_u^+$ state should show a curve which at moderately large R rises with decreasing R roughly as fast as the 2440 curve falls. In I_2, the situation is complicated by the fact that the 1441, $^3\Sigma_u^+$ state splits into two substates with $\Omega = 0^-$ and 1, respectively, of which according to Table I the 0_u^- dissociates to $^2P_{3/2} + ^2P_{3/2}$, and the 1_u to $^2P_{3/2}$ plus $^2P_{1/2}$ atoms. Because of this difference the 0_u^- curve should rise somewhat *more* and the 1_u curve somewhat *less* steeply from its asymptote than if the ^2P splitting were negligibly small. Figure 1 is drawn accordingly.[9] Another point is the following: From the absorption spectrum of I_2 (see Sec. VI) it is possible to deduce the *slope* of the $^3\Sigma_u^+$ curves at R equal to R_e of X; Fig. 1 has been drawn accordingly.

In the 2440, $^1\Sigma_g^+$ state the descent of the potential curve to a stable minimum is correlated with the presence of two electrons in the σ_g bonding MO. The eight π_u and π_g electrons (and the two pairs of $5s$ electrons) have net antibonding effects, but at R_e these are not yet dominant. This is because the overlap in the LCAO expression for σ_g, namely, $5p\sigma + 5p\sigma$, is more long range than that for the other valence-shell MO's ($\pi_{u,g} \approx 5p\pi \pm 5p\pi$ and $\sigma_{g,u} = 5s \pm 5s$). The $5s$ and $5p\pi$ shells, however, exercise a restraining influence which prevents R_e from being smaller than it is.

In the 2431 group of states ($\sigma_g^2 \sigma_u$ and $\pi_u^4 \pi_u^3$), bonding effects predominate over antibonding effects. This is best seen by referring the energies of these states to a dissociation asymptote at the center of gravity of the atomic state pairs $^2P_{3/2} + ^2P_{3/2}$, $^2P_{3/2} + ^2P_{1/2}$, and $^2P_{1/2} + ^2P_{1/2}$. This center of gravity is located at an energy two-thirds of the distance up from $^2P_{3/2} + ^2P_{3/2}$ toward $^2P_{3/2} + ^2P_{1/2}$. If referred to it, all the 2431 states should have pronounced minima. The fact that only the $^3\Pi_{0^+u}$ state with dissociation asymptote $^2P_{3/2} + ^2P_{1/2}$ has a fairly deep minimum is a result of the intraatomic spin–orbit coupling which depresses the dissociation asymptote $^2P_{3/2} + ^2P_{3/2}$ of the other states. (However, the $^3\Pi_1$ and $^3\Pi_2$ states have shallow minima.)

In the 2341 set of states, the $\sigma_g^2 \sigma_u$ grouping should exert a bonding effect which should predominate at medium-large R values making the 2341 curves relatively flat at large R values. They have been drawn accordingly in Fig. 1. Their rise to higher vertical energies at R_e of state X must be attributed to the antibonding action of the $\pi_u^3 \pi_g^4$ grouping.

In the 2422 states and in the 2332 states which dissociate to neutral atoms, the grouping $\sigma_g^2 \sigma_u^2$ which is present should exert a strong antibonding effect at medium-large R values; and the potential curves have been drawn accordingly. It is assumed that the antibonding effect is about the same as in the 1441, $^3\Sigma_u^+$ states.[10]

In all the states of category (1), the long-range forces should give rise to shallow minima and in some cases small maxima in the range 4–5 Å. The corresponding energies consist in London dispersion potentials going as R^{-6} and in quadrupole–quadrupole attractions or repulsions going as R^{-5}. The latter should lead to small splittings of potential curves at large distances, given by the formula[8]

$$U_Q(R) = a\langle r^2 \rangle^2 / R^5, \qquad (1)$$

where $\langle r^2 \rangle$ is the mean squared radius of the iodine atom, and the coefficient a varies from one state to another. The U_Q contributions to $U(R)$ are too small to be shown in Fig. 1. However, a listing of values of $a\langle r^2 \rangle$ for various states, given in Table II, based on Ref. 8, will serve to indicate how the curves should go at large R.[11,12]

LeRoy,[13] on the basis of a reinterpretation of data of Verma, has concluded that a repulsive state of 0_g^+ case c character, which he identifies as 2341, $^3\Pi_{0^+g}$, has a small maximum at about 8.7 Å due to quadrupole–quadrupole repulsive forces, with a London dispersion force minimum at about 6 Å. According to Table I, LeRoy's state may be 2422, $^3\Sigma_g^-(0^+)$ instead of 2341, $^3\Pi_{0^+g}$; however, the estimated vertical energy of the latter is only 0.3 eV above that of the former in Table I, and a reversed order is almost as likely as not. Actually, at large R values the wavefunction must be a case c mixture of these and other (2440 and 2422, $^1\Sigma_g^+)0_g^+$ wavefunctions.

LeRoy and Bernstein[3d] have shown that the high vibrational levels of the 2431, $^3\Pi_{0^+u}(B)$ state indicate that the potential curve at large R is approximately of

the form C/R^5 with $C=-3.11\times10^5$, in approximate agreement with the predicted value -4.54×10^5 given in Table II.

For the states in category (2), complete potential curves have been drawn in Fig. 1 only in a few cases. It is difficult to decide how the curves should be drawn with respect to dissociation products. The experimentally well-established states E and F, here, respectively, assigned as 1432, $^3\Pi_{0^+g}$ or 2242, $^1\Sigma_g^+$, and 2332, $^1\Sigma_u^+$, have low ω_e values, which shows that they are of essentially ionic character (see Secs. VI, VII) and indicates that they tend to dissociate into $I^+(\cdots5p^4, {}^3P$ or ^1D or $^1S)$ plus $I^-(\cdots5p^6, {}^1S)$. One may then ask, should this tendency be observed with respect only to the case c character $(0_g^+, 0_u^-, 1_g, 1_u,$ etc.) of the states, or should formally triplet and singlet states of I_2 tend to dissociate, respectively, to triplet or singlet states of I^+? In Table I and Fig. 1, dissociation products corresponding to the first of these alternatives have been assumed, but in addition, the dissociation products which would correspond to the second alternative have been given in Table I in parentheses.

However, at least many of the states of category (2), after making an approach toward dissociation into ions, actually must shortcut, as required by the rigorous noncrossing rule, into one or another state pair in which one atom is in the ground state configuration and the other atom in a Rydberg state. The lowest energy of such state pair is $\cdots5p^5, {}^2P_{3/2}$ plus $\cdots5p^46s, {}^4P_{5/2}$ with an energy of 8.29 eV, as compared with the lowest-energy ion pair $\cdots5p^4, {}^3P_2$ plus $\cdots5p^6, {}^1S$ with an energy of 8.65 eV (both relative to the ground state of I_2). In Table I and Fig. 1, however, dissociation is shown as if always into ions.

IV. PREDISSOCIATIONS OF THE 2431, $^3\Pi_{0^+u}(B)$ STATE

Of the states of the 2431 configuration, the B state is the best known. A number of interesting papers have been published recently[3,14–26] concerning this state and its predissociation into other states which have repulsion curves. It is known that direct absorption occurs to the 2431, $^1\Pi_u$ repulsion state[26] but also that spontaneous predissociation to this state from the B state occurs.[16,22,23] From the variation of spontaneous predissociation with vibrational quantum number in the B state, Chutjian[17] has deduced the approximate location of the $^1\Pi_u$ potential curve. It appears that the $^1\Pi_u$ curve lies close to the B curve in the region of all but the lowest vibrational levels of the latter, and probably crosses it at an R value slightly greater than R_e of state X (see Sec. V). Figure 1 has been drawn accordingly.

It has been shown[27,24] experimentally that fluorescence from the B state is quenched by a strong magnetic field. Turner[27] suggested that the effect is an induced predissociation, and Van Vleck[28] showed theoretically that a magnetic field *should* cause predissociation into some state of 0_u^- character, probably the

TABLE II. Coefficients of R^{-5} in Eq. (1),[a,b] in cm^{-1} Å.[5]

State[c]	Coeff.$\times10^{-5}$	State[d]	Coeff.$\times10^{-5}$
2440, $^1\Sigma_g^+$	0.00	2431, Π_{0^+u}	−4.51
2431, $^3\Pi_{2u}$	−2.64	2341, $^3\Pi_{0^+g}$	+4.51
2431, $^3\Pi_{1u}$	−0.76	2341, $^3\Pi_{0^-g}$	0.00
2431, $^3\Pi_{0^-u}$	−0.76	2341, $^1\Pi_g$	−3.00
2431, $^1\Pi_u$	+1.13	2422, $^3\Sigma_g^-(1)$	0.00
2341, $^3\Pi_{2g}$	+0.38	2422, $^1\Delta_g$	+0.75
2341, $^3\Pi_{1g}$	−1.51	2422, $^1\Sigma_g^+$	0.00
1441, $^3\Sigma_u^+(0^-)$	+3.02	1441, $^3\Sigma_u^+(1)$	+3.00
2422, $^3\Sigma_g^-(0^+)$	+2.26	2332, $^2\Delta_{2u}$	−0.75
2332, $^3\Delta_{3u}$	+1.13	2332, $^3\Delta_{1u}$	0.00
		2332, $^1\Sigma_u^-$	0.00
		2332, $^3\Sigma_u^+(0^-)$	0.00
		2332, $^3\Sigma_u^+(1)$	0.00

[a] Based on Ref. 8; Eqs. (3.56a) and (3.57), and Tables II, IV, and VII.
[b] See Ref. 11.
[c] States dissociating to $^2P_{3/2}+{}^2P_{3/2}$.
[d] States dissociating to $^2P_{3/2}+{}^2P_{1/2}$ or $^2P_{1/2}+{}^2P_{1/2}$.

2431, $^3\Pi_{0^-u}$ repulsion curve or possibly a $^3\Sigma_u^+(0^-)$ curve. For the latter there are two possibilities, the 1441, $^3\Sigma_u^+(0^-)$ and the 2332, $^3\Sigma_u^+(0^-)$ repulsion curves; there is also a fourth 0_u^- repulsion curve, that of the 2332, $^1\Sigma_u^-$ state. To cause predissociation, the 0_u^- curve in question must either come very near to, or cross, the B state curve. According to Table I and Fig. 1, the $^3\Pi_{0^-u}$ curve lies fairly close below the B curve and the 1441, $^3\Sigma_u^+$ curve crosses the B curve, while the other two 0_u^- curves dissociate to give one or both atoms excited and so do not cross the B curve. However, since the energy estimates in Table I *are* only estimates, there is a small possibility that it is the 2332, $^1\Sigma_u^-$ or the 2332, $^3\Sigma_u^+(0^-)$ curve instead of the 1441, $^3\Sigma_u^+(0^-)$ curve which crosses the B curve.

Turner studied dependence of the magnetic predissociation efficiency on the quantum number v of the B state vibrational levels. Degenkolb et al.[24] obtained similar but more accurate results. The magnetic predissociation sets in gradually at low v values, rises to a maximum near $v=23$, and then falls gradually with increasing v (see their Fig. 10). As Degenkolb et al. point out, the gradual rise at low v values is not in agreement with what would be expected if the predissociation is due to a crossing of the B curve by a 0_u^- curve on the former's *outer* (large R) limb. For such a crossing [which, according to Fig. 1 actually occurs, by the 1441, $^3\Sigma_u^+(0^-)$ curve] one would expect on Franck–Condon considerations a very rapid rise of the predissociation just before the crossing, followed perhaps by a gradual falling off at higher v. Degenkolb et al. then conclude that there is a crossing on the *inner* limb of the B curve, and deduce therefrom a segment of the predissociating 0_u^- curve (see their Fig. 11). This they identify with the 2332, $^3\Sigma_u^+(0^-)$ state.[29] In another paper,[25] Huo concludes that the crossing point of the two curves is at about $v=18$, which corresponds to an energy of 17 850 cm^{-1} on Fig. 1 and an R value of 2.73 Å.

However, a potential curve crossing the B curve at this point is totally inconsistent with the estimates of vertical energy, at R_e of the ground state, for 2332, $^3\Sigma_u{}^+(0^-)$ or for either of the alternative possible $0_u{}^-$ states mentioned above, of which in this writer's opinion the 1441, $^3\Sigma_u{}^+(0^-)$ is most probably the lowest. Such a curve would have to go up almost vertically according to Fig. 1. Unless the basis of Table I, and the considerations used in drawing the curves in Fig. 1 (see especially Sec. III) are completely wrong, it appears to be necessary to find an alternative to the interpretation of the magnetic predissociation efficiency curves given by Degenkolb *et al.* and by Huo. The most obvious alternative is that the predissociating $0_u{}^-$ curve deduced by Degenkolb *et al.* is correct but belongs to the 2431, $^3\Pi_0{}^-{}_u$ state. This seems to be a possibility and is in accord with Van Vleck's theory. However, the writer has given strong reasons[1b] for believing that the 2431, $^3\Pi_0{}^-{}_u$ curve runs below and does not cross the $^3\Pi_0{}^+{}_u$ curve; these reasons will be reviewed in Sec. V below.

The following alternative explanation then seems highly probable. Assuming that the $^3\Pi_0{}^-{}_u$ curve runs slightly to the left of the $^3\Pi_0{}^+{}_u$ as shown in Fig. 1, the nuclear wavefunctions of the former overlap the vibrational wavefunctions of the latter increasingly as the quantum number v increases from zero; at $v=0$ there should be little overlap since the two curves are relatively far apart. These predicted relations are consistent with the observed increase in magnetic predissociation efficiency up to say $v=20$. After that, the observed efficiency soon comes to a maximum and then decreases. Qualitatively at least, this behavior can be explained as follows. The distance between the $^3\Pi_0{}^-$ and $^3\Pi_0{}^+$ curves is now nearly constant, so one might argue that the predissociation efficiency should reach and stay on a plateau. But above about $v=20$ a new factor enters, namely the potential curve of the B state is becoming increasingly asymmetrical—steeper on the inner limb and flatter on the outer limb. Correspondingly, the first maximum of the vibrational wavefunction, just inside the inner limb, on whose overlap with the first maximum of the continuum function of the $^3\Pi_0{}^-$ state the predissociation efficiency depends, becomes lower while the last maximum just before the outer limb becomes higher and broader. This effect[30] is a large one at higher v values and, while, of course, the matter needs to be checked quantitatively, it appears adequate to account for the passage of the efficiency through a maximum followed by a steady falloff at high v values, as observed.

Granting the foregoing as the *basic* explanation, it is possible that crossing of the outer limb of the B curve by a $0_u{}^-$ curve also contributes appreciably to the magnetic predissociation efficiency. In Fig. 1, the 1441, $^3\Sigma_u{}^+(0^-)$ curve crosses the B curve at about $v=10$. This crossing,[31] which must certainly occur *somewhere*, actually must make *some* contribution to the predis-

sociation efficiency, and may perhaps contribute appreciably *to the observed maximum*, even though for reasons discussed above it cannot account for the gradual rise of the efficiency curve at low v values.

To summarize, the magnetic predissociation of the B curve is caused mainly by the 2431, $^3\Pi_0{}^-{}_u$ state, assisted somewhat by (most probably) the 1441, $^3\Sigma_u{}^+(0^-)$ state; the $^3\Pi_0{}^-{}_u$ curve possibly may cross the B curve, but most probably runs entirely below it.

Besides spontaneous predissociation to 2431, $^1\Pi_u$ and magnetically induced predissociation, predissociation of the B state is induced by collisions.[15,18–24,32] Induced predissociation is signalized by "quenching" of the fluorescence of the B state; in the absence of disturbing influences, the absorption process $B\leftarrow X$, where X is the ground state, is followed by the radiative reverse process $B\rightarrow X$. The extent of collision quenching by foreign gases increases with vibrational quantum number,[32,19,21] but in the case of self-quenching ($I_2{}^*$ by I_2) Chutjian *et al.*[16] find that there is very little variation with v. Selwyn and Steinfeld[20,21] have concluded on theoretical grounds that collisional quenching should take place by predissociation to repulsion state curves crossing the B state potential curve only in the case of states to which the selection rules for radiative transitions from B would apply. The only important such state[33] is the 2341, $^3\Pi_0{}^+{}_g$, and Steinfeld attributes the collision quenching to predissociation into this state.[34] However, the potential curve of this state is not suitably located in Fig. 1; but if the estimated vertical positions of 2341, $^3\Pi_0{}^+{}_g$ and 2422, $^3\Sigma_g{}^-(0_g{}^+)$, which *does* cross the B curve in Fig. 1, were interchanged, as it is not unlikely they should be,[35] the 2341, $^3\Pi_0{}^+{}_g$ curve, which would be the curve of a state discussed by LeRoy [see paragraph immediately following Eq. (1)], would cross the B curve at low v values and may well be responsible for collisional predissociation.

V. THE 2431 FAMILY OF STATES

The iodine absorption spectrum in the visible region consists of transitions to the $^3\Pi_{1u}(A)$, $^3\Pi_0{}^+{}_u(B)$, and $^1\Pi_u$ states of the 2431 family. A discussion of the relative intensities of these transitions, and related calculations on the positions of the individual states of the 2431 configuration, have been given previously.[1b] On the basis of new data, a revision of this discussion is needed, and is given here. A critical discussion of some other points raised by various authors is also included.

In Ref. 1(b), the positions of the vertical energies at R_e of state X were based for $^3\Pi_{1u}$ and $^3\Pi_0{}^+{}_u$ on experimental ν_{max} values of the dissociation continuum associated with these transitions, and the vertical energies of the $^1\Pi$, $^3\Pi_0{}^-$, and $^3\Pi_2$ states were calculated. Two possibilities were considered, called interpretations I and II, based on the assumption of a singlet–triplet separation parameter X of 3500 or 1000 cm^{-1}, respectively, of which the former seemed the more probable. Formerly ν_{max} for $^3\Pi_1\leftarrow X$ was taken as 13 660

cm^{-1} [cf. Table II of Ref. 1(b)] but more recent experimental data give a higher value. For iodine in solution in heptane, Ham[36] finds 14 600±300, while Mathieson and Rees[37] in the vapor find about 14 400 cm^{-1}; Tellinghuisen[38] obtains rather strong evidence for a value of at least 15 000 cm^{-1} in the vapor; let us take 15 000 cm^{-1}.

We now proceed in a somewhat different way than in Ref. 1(b). Previously there was no direct information as to the location of the $^1\Pi$ state, but the work of Chutjian[17] (see first paragraph of Sec. IV) made it probable that ν_{max} for $^1\Pi\leftarrow X$ is roughly the same as the value (19 200 cm^{-1}) for ν_{max} of $^3\Pi_{0^+}\leftarrow X$. However, Wilson et al.[26b] on the basis of photofragment spectroscopy data have obtained about 20 300 cm^{-1} for ν_{max} of $^1\Pi\leftarrow X$ and about 19 000 cm^{-1} for ν_{max} of $B\leftarrow X$. Let us try each of two assumptions: (1), $\nu_{max}=19\ 200$ the same for $^1\Pi\leftarrow X$ and $B\leftarrow X$; (2), $\nu_{max}=20\ 300$ cm^{-1} for $^1\Pi\leftarrow X$. Assumption (1) makes the $^1\Pi_u$ curve cross the $^3\Pi_{0^+u}$ curve at R_e of state X, at a frequency considerably below that (about 20 000 cm^{-1}) of the convergence point of the vibrational levels of the B state. Chutjian's calculations (which indicate the possibility of only weak predissociation of the B by the $^1\Pi_u$ state if the $^1\Pi_u$ curve is very close to the B curve, even if it has crossed the latter) seem to invalidate the argument given previously[1b] that the $^1\Pi_u$ curve cannot cross the B curve until a point above the convergence limit of the latter is reached. (It was argued[1b] that if a crossing had occurred, fluorescence from the B state vibrational levels lying at higher energies would not have been observed, whereas actually fluorescence from vibrational levels almost[3b] up to convergence is observed.) Assumption (2) makes the $^1\Pi$ curve cross the B curve even lower, at an R value a little greater than R_e of X.

Theoretically the energies of $^3\Pi_1$ and $^1\Pi$ are given[1b] by

$$E=E_0\pm\tfrac{1}{2}(X^2+a^2)^{1/2},\qquad (2)$$

where a is the spin–orbit coupling coefficient, whose value is known from the atomic spectrum to be 5067 cm^{-1}. According to Eq. (2), the energy interval $\Delta\nu=E(^1\Pi)-E(^3\Pi_1)$ is $(X^2+a^2)^{1/2}$. Knowing $\Delta\nu$ and a, X can be calculated. However, the vertical energies (ν_{max}) of 19 200 by assumption (1) [or 20 300 by assumption (2)] and 15 000 for $^1\Pi$ and $^3\Pi_1$ must first be corrected for Type I case c perturbations. It is the unperturbed energies which should be used in Eq. (2).

Type I case c interactions are discussed in Ref. 1(a). They arise from the fact that there is a partial persistence of intraatomic spin–orbit coupling in the molecule. Using Heitler–London theory and neglecting overlap, Van Vleck[28] has given secular equations for the estimation of these case c effects in $\Omega=0$ states, and in Ref. 1(b) corresponding second-order perturbation expressions are given for $\Omega=0$ and 1 states. These Type I case c interactions must cause energy depressions of all the 2431 states except for $^3\Pi_{0^+}$. The magnitudes of these

depressions of all the 2431 states except for $^3\Pi_{0^+}$. The magnitudes of these depressions for $\Omega=0$ and 1 states have been estimated in Table IV of Ref. 1(b) but require some revision because of the altered estimates of vertical energy for the perturbing states in the present Table I as compared with the earlier estimates in Ref. 1(a). For the $^3\Pi_1$ and $^1\Pi$ states, the previous estimates of the energy depressions were 688 cm^{-1} for $^3\Pi_1$ and 2280 cm^{-1} for $^1\Pi$. Revised estimates obtained in the same way as before but using the new vertical energies from the present Table I are 550 and 1910 cm^{-1}, respectively.[39] While these values cannot be relied on as exact because of the Heitler–London approximation used neglecting overlap, they should be useful for an estimate. Adding these corrections to the ν_{max} values, one obtains for the unperturbed $^1\Pi$ and $^3\Pi_1$ energies the respective values 21 110 (or 22 210) and 15 550 cm^{-1}. From their average, the (unperturbed) E_0 of Eq. (2) is 18 325 (or 18 880) cm^{-1}. From their difference, 5560 (or 6660) cm^{-1}, using Eq. (2) with $a=5067$, one obtains $X=2300$ (4320) cm^{-1}. These values are near that (3500 cm^{-1}) assumed in Interpretation I in Ref. 1(b).

Given X and a and the mean value E_0 (18 330 or 18 880 cm^{-1}) of the unperturbed $^3\Pi_1$ and $^1\Pi$ states, the positions of the unperturbed $^3\Pi_{0^\pm}$ and $^3\Pi_2$ states can be computed, and from these, after applying case c corrections, estimates of the actual positions of these states can be made. Also, the intensity of the $^1\Pi\leftarrow X$ transition can be calculated from that of the $3\Pi_1\leftarrow X$ transition. For the latter, the ratio of the dipole strengths $D(^1\Pi)/D(^3\Pi_1)$ is given[1b] by

$$D(^1\Pi)/D(^3\Pi_1)=[R+(R^2+1)^{1/2}]^2,\qquad (3)$$

where $R=X/a$. Here $R=2300/5067=0.453$ (or $4320/5067=0.852$), giving $D(^1\Pi)/D(^3\Pi_1)=2.38$ (or 4.66). Using the approximate experimental value[40] $2D(^3\Pi_1)=19\times10^{-4}$ (in angstroms^2), we find $2D(^1\Pi)=45.1\times10^{-4}$ (or 89.3×10^{-4}).[41] The corresponding oscillator strengths given by $f=1.096\times10^{-5}$ $(2D\nu)$ if D is in angstroms^2 and ν in cm^{-1}, using $\nu=15\ 000$ and 19 200 (or 20 300), respectively, are 3.12×10^{-4} and 0.95 (or 1.99)$\times10^{-3}$.

The absorption with peak at 19 200 cm^{-1}, now interpreted as a superposition of $^3\Pi_{0^+}\leftarrow X$ and $^1\Pi\leftarrow X$, has a total D of about 620×10^{-4} Å^2. Subtracting the dipole strength 45 (or 89)$\times10^{-4}$ for $^1\Pi\leftarrow X$, there remains 575 (or 531)$\times10^{-4}$ Å^2 attributable to $^3\Pi_{0^+}\leftarrow X$[41]; this corresponds to an oscillator strength 1.21 (or 1.11)$\times10^{-2}$. On the basis of these calculations, the $^1\Pi\leftarrow X$ absorption, which must be entirely continuous, makes up about 7% (or 15%) of the total (banded plus continuous) absorption in the λ 5200 region of the iodine absorption spectrum. Direct estimates[17,26] of the $^1\Pi_u\leftarrow X$ continuum absorption observed between the band lines of the $^3\Pi_{0^+}\leftarrow X$ transition, amount to about 20%±10% of the total, or[26b] perhaps about 30% of the total. On the whole, it appears that preference should

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TABLE III. Vertical energies of 2431 states (cm⁻¹).

State	Unpert. energy	Calc Type I case c pert.	Perturbed energy
$^1\Pi$	22 210	−1910	20 300[a]
$^3\Pi_{0^+}$	19 250[b]	0	19 000[a]
$^3\Pi_{0^-}$	19 250[b]	−1980	17 270[b]
$^3\Pi_1$	15 550	−550	15 000[c]
$^3\Pi_2$	14 185[b]	(−420)	13 765[b]

[a] Approximate observed ν_{max} on the basis of Ref. 26(a). Calculated, 19 250.

[b] Calculated using data on $^3\Pi_1$ and $^1\Pi$ states.

[c] Approximate ν_{max} based on Tellinghuisen.[38]

be given to assumption (2). Pending further experimental work, it seems justifiable to conclude tentatively that about 20% of the intensity of the absorption with peak at 19 200 cm⁻¹ can be attributed to the $^1\Pi_u \leftarrow X$ transition.

The predicted locations of the vertical energies of $^3\Pi_0^-$, $^3\Pi_0^+$, and $^3\Pi_2$ are now obtained as follows. First the *unperturbed* locations of the $^3\Pi_0^+$ and $^3\Pi_0^-$ states are obtained from the relation[1b]

$$E(^3\Pi_0) = E_0 - \tfrac{1}{2}X + \tfrac{1}{2}a, \qquad (4)$$

using the unperturbed E_0 value of 18 880 from assumption (2). The result is 19 250 cm⁻¹ for the unperturbed location of $^3\Pi_0$. For the $^3\Pi_0^+$ substate there is no Type I case c depression. For $^3\Pi_0^-$ the Type I case c depression, given previously[1b] as 2420 cm⁻¹, is now computed to be 1980 cm⁻¹. The predicted actual location of $^3\Pi_0^-$ is then 19 250 − 1980 = 17 270 cm⁻¹. For $^3\Pi_2$, the unperturbed location is given by $E_0 - \tfrac{1}{2}X - \tfrac{1}{2}a = 14\ 185$ cm⁻¹; with an estimated Type I case c correction of 420 cm⁻¹, the predicted actual location is 13 765 cm⁻¹.

The results of the preceding calculations on vertical energies for assumption (2) are summarized in Table III. It will be noted that the calculated $^3\Pi_0^+$ energy differs slightly from the observed. This is the only *calculated* energy for which there is an experimental check. Deviations from the calculated perturbed energies are expected since the calculated quantities are only approximate, and the calculations do not fully take into account all interactions. The calculation indicates that the $^3\Pi_0^-$ potential curve, which dissociates to $^2P_{3/2} + ^2P_{3/2}$, runs almost 2000 cm⁻¹ below the $^3\Pi_0^+$ curve at R_e of state X. As discussed in Sec. IV, there seems to be no doubt that the observed magnetic predissociation of the $^3\Pi_0^+$ state is due mainly to the $^3\Pi_0^-$ state. However, Van Vleck[28] states that this magnetic predissociation cannot be important if the $^3\Pi_0^-$ state is more than about 1000 cm⁻¹ below the $^3\Pi_0^+$ state. It therefore seems probable that the $^3\Pi_0^-$ state, although below the $^3\Pi_0^+$ state as indicated by Table III, is considerably closer to the latter than Table III indicates; Fig. 1 has been drawn accordingly.

In the preceding discussion the "unperturbed" values

for the energies of the various states of the 2431 configuration have taken into account only Type I case c depression of the energies. But there is also configuration interaction with higher-energy states, most notably with the states of 1342 configuration. However, the interaction of corresponding states of the two configurations ($^3\Pi_2$ with $^3\Pi_2$, $^3\Pi_1$ with $^3\Pi_1$, and so on) should be nearly the same for all such pairs of states, so that there should be no important net effect on the relative energies of the various 2431 states, and our previous discussion does not need to be modified on account of it, since any gross effect is already included in the experimental values of the $^1\Pi_u$ and $^3\Pi_{1u}$ states.

Nevertheless, this configuration interaction indirectly introduces some "Type II" case c interactions,[1b] in particular through Type I case c interaction of 1342, $^3\Pi_{0^+u}$ with 1441, $^1\Sigma_u^+$. Thereby, through strong configuration interaction of 1342, $^3\Pi_{0^+u}$ with 2431, $^3\Pi_{0^+u}$, some admixture of 1441, $^1\Sigma_u^+$ is brought into the latter. To this admixture may be attributed some of the intensity of the $B \leftarrow X$ bands, but not very much (see below). However, another major part must be attributed to the Type I case c admixture of 2341, $^3\Pi_{0^+g}$ into the 2440, $^1\Sigma_g^+$ state X since the transition 2431, $^3\Pi_{0^+u} -$ 2341, $^3\Pi_{0^+g}$ is strongly allowed. This question has been discussed previously,[28,1b] but the matter can be further clarified. The perturbed wavefunction of state X is

$$\Psi(X) \approx \Psi_0(X) - [a/(H_{22} - H_{11})]\Psi_0(2341, {}^3\Pi_{0^+g})$$
$$+ \cdots \approx \Psi_0(X) - 0.153\Psi_0({}^3\Pi_{0^+g}), \quad (5)$$

where $H_{22} - H_{11} = 33\ 200$ cm⁻¹ according to Table I. The dipole moment of the $B \leftarrow X$ transition due to this perturbation of X is easily seen to be

$$D(2431, {}^3\Pi_{0^+u} \leftarrow X)$$
$$= [a/(H_{22} - H_{11})]^2 D(2341, {}^3\Pi_{0^+g}; 2431, {}^3\Pi_{0^+u}). \quad (6)$$

Now the transition between the $^3\Pi_{0^+g}$ and $^3\Pi_{0^+u}$ states is a one-electron transition analogous to that between the lowest $^2\Sigma_g^+$ and $^2\Sigma_u^+$ states of H_2^+ or He_2^+, for which the simple LCAO approximation to D is[42]

$$D = R^2/4(1 - S^2). \qquad (7)$$

Using an estimated value of 0.05 for S^2 and putting $R = R_e$ of state X of $I_2 = 2.67$ Å, Eq. (7) gives 1.87 Å². The calculated contribution of the admixture of 2341, $^3\Pi_{0^+g}$ in X to the intensity of the $B \leftarrow X$ transition is then $(0.153)^2 \times 1.87 = 0.0442$ Å². Since LCAO calculations usually give an overestimate,[42] one may perhaps estimate a contribution of 0.03 Å² to the dipole moment of $B \leftarrow X$. (This corresponds to $D({}^3\Pi_{0^+g}; {}^3\Pi_{0^+u}) = 1.28$ Å².) Since the total dipole moment of $B \leftarrow X$ is about 0.053 Å² (see above), there remains about 0.023 Å² which we may try to account for by the $^1\Sigma_u^+$ perturbation of state B.[43]

To see whether 0.023 Å² of the dipole strength of $B \leftarrow X$ can be reasonably explained in this way, let ψ_1, ψ_2, and ψ_3 be the wavefunctions of the states 2431,

$^3\Pi_{0^+u}(B)$; 1441, $^1\Sigma_u^+$; and 1342, $^3\Pi_{0^+u}$. Then,[44] approximately,

$$\Psi_B \equiv \Psi_1 = \Psi_1^0 - [H_{13}/(H_{33}-H_{11})]\Psi_3 + \cdots,$$

$$\Psi_3 = \Psi_3^0 + [H_{23}/(H_{33}-H_{22})]\Psi_2^0 + \cdots. \quad (8)$$

Putting $H_{23}=a=5067$ cm^{-1}, $H_{33}-H_{22}=30\,000$ cm^{-1}, and $H_{33}-H_{11}=61\,000$ cm^{-1} (see Table I), let us take $H_{13}=25\,000$ cm^{-1} as a trial assumption. H_{13} can scarcely be any larger than this. Then (after normalization),

$$\Psi_B = 0.916\Psi_1^0 - 0.378\Psi_3^0 - 0.064\Psi_2^0. \quad (9)$$

To calculate the dipole moment of the transition $B \leftarrow X$ due to the combined effects of 1441, $^1\Sigma_u^+$ admixture in state B and $^3\Pi_{0^+g}$ admixture in state X, one writes $D(B, X) = [\int \Psi_B(\sum z_i)\Psi_X dv]^2$ and substitutes for Ψ_B from Eq. (9) and for Ψ_X from Eq. (5). The result is

$$D(B, X) = (0.064)^2 D(\Psi_2, \Psi_X) + 2(0.064)(0.916)(0.153)[D(\Psi_2, \Psi_X)D(\Psi_1^0, \Psi(^3\Pi_{0^+g}))]^{1/2}$$

$$+ (0.916)^2(0.153)^2 D(^3\Pi_{0^+g}, {}^3\Pi_{0^+u}) = 0.0041 D(1441, {}^1\Sigma_u^+ \leftarrow X)$$

$$+ 0.0178[D(1441, {}^1\Sigma_u^+ \leftarrow X)D(2341, {}^3\Pi_{0^+g}; 2431, {}^3\Pi_{0^+u})]^{1/2}$$

$$+ 0.0192 D(2341, {}^3\Pi_{0^+g}; 2431, {}^3\Pi_{0^+u}). \quad (10)$$

Now $D(1441, {}^1\Sigma_u^+ \leftarrow X)$ in square angstroms is approximately 0.72.[45] Substituting this and the estimated $D(^3\Pi_{0^+g}, {}^3\Pi_{0^+u})$ of 1.28 Å^2 into Eq. (10), the three terms become 0.0030, 0.0171, and 0.0246, or a total of 0.045. Thus, although the $^1\Sigma_u^+$ admixture in the B state by itself contributes directly only 0.0030 to $D(B, X)$, its participation in the cross term in Eq. (10) makes a very substantial contribution (here estimated as 0.017), which together with the major direct contribution (0.0246) due to the admixture of 2341, $^3\Pi_{0^+g}$ into X accounts to a large extent for the observed $D(B, X)$ of 0.053 Å^2. Exact agreement would be obtained if $D(2341, {}^3\Pi_{0^+g}; 2431, {}^3\Pi_{0^+u})$ is somewhat larger than estimated, or by minor modifications of some of the other estimated quantities.

VI. THE ULTRAVIOLET ABSORPTION SPECTRUM AND THE 1441 CONFIGURATION

The room temperature uv absorption spectrum of iodine vapor consists of a very weak but broad continuum with maximum near 2700 Å, followed by a very intense and extensive banded region with maximum at 1825 A, and at somewhat shorter wavelengths sharp Rydberg series bands. For an over-all view, see Figs. 1 and 2 of a paper by Myer and Samson.[47] It was suggested long ago[1a,42] that the extensive system with maximum at 1825 Å (the D bands) corresponds to the transition 1441, $^1\Sigma_u^+(D) \leftarrow X$. Although differing proposals have been made,[37,48,49] there can be no reasonable doubt of the identification just given as corresponding to at least the major part of the absorption with peak at 1825 Å (see below). The Rydberg bands have been photographed at high resolution and analyzed in a paper by Venkateswarlu,[50] but will not be discussed here.

The ν_{max} corresponding to 1825 Å is 6.77 eV, while that corresponding to 2700 Å is 4.57 eV.[51] The difference, of 2.2 eV, is very reasonable for the energy interval between the $^1\Sigma_u^+$ and $^3\Sigma_u^+$ states of the 1441 configuration. It has been shown conclusively[52] that the continuum near 2700 Å is a superposition of two transitions, one belonging to I$_1$. The remaining absorption may be identified with high probability as going to the 1_u component of 1441, $^3\Sigma_u^+$, as is allowed in case c, with intensity acquired mainly by case c mixing of $^3\Sigma_u^+(1)$ with 2431, $^1\Pi_u$. The attribution of this transition to 2332, $^3\Sigma_u^+(0^-) \leftarrow X$ as proposed by Mathieson and Rees[37] must be rejected because $0_u^- \leftarrow 0_g^+$ transitions are too highly forbidden.[53] However, the segment of $U(R)$ curve deduced for R near R_e of state X by Mathieson and Rees for the upper state of the transition can be accepted and is used in Fig. 1 but attributed to 1441, $^3\Sigma_u^+(1)$. A similar behavior of the 1441, $^3\Sigma_u^+(0^-)$ curve, but with a slightly different vertical energy and a lower dissociation asymptote (see Table I), is assumed in Fig. 1.

The only other possibilities than 1441, $^3\Sigma_u^+(1)$ which could be considered for the upper state of the λ 2700-Å transition are 2332, $^3\Delta_{1u}$, $^3\Sigma_u^+(1)$, and $^3\Sigma_u^-(1)$, which, however, are estimated to have higher energy (see Table I) so that the case-c-allowed weak transitions to these levels are most probably hidden under the strong D$\leftarrow$X bands. However, just possibly one or two of them may be represented in the very broad λ 2700-Å transition along with 1441, $^3\Sigma_u^+(1) \leftarrow X$.

For a correct interpretation of the extensive system of absorption bands with maximum at about 1825 Å observed at room temperature (the "feinkannelliertes Bandensystem" of Cordes,[54] which hereafter will be referred to as the Fk Cordes bands), one may rely on a confrontation of experiment and theory, with emphasis on intensity as well as frequency. Theoretically, the by far strongest transition which can be considered is 1441, $^1\Sigma_u^+$–2440, $^1\Sigma_g^+$. This belongs to the class of intense NV transitions, with an essentially ion-pair type of upper state which should have a low vibration

frequency ω_e and relatively large equilibrium separation R_e and of which the $\sigma_g 1s\sigma_u 1s$, $^1\Sigma_u^+\leftarrow\sigma_g 1s^2$, $^1\Sigma_g^+(V\leftarrow N)$ transition of H_2 is the prototype.[42] A very extensive system of bands is predicted, fading out at its long-wavelength end because of the Franck–Condon principle, so that the 0, 0 band is not detectable in room-temperature absorption. All this is exactly what is observed. Moreover, at higher temperatures and pressures, the system of absorption bands spreads toward longer wavelengths, exactly as expected by the Franck–Condon principle due to absorption from higher levels of vibration of state X. The additional, "PR and KM," bands[55] together with the Fk Cordes bands have been analyzed as a single system by several investigators.[56–58]

For an estimation of the intensity of the bands, perhaps the best value[60] is that of Julien and Person,[46] who for the vapor, pressurized[61] in an atmosphere of nitrogen to remove the fine structure, report an oscillator strength $f = 0.43$ with an error estimated[61] at $\pm 20\%$. The pressurized absorption curve of Julien and Person shows a single peak.

On the other hand, Figs. 1 and 2 of a paper by Meyer and Sampson,[47] which give an instructive panorama of the bands at low pressure, show two maxima with somewhat smaller absorption between them.[62] The two maxima can be understood as a Franck–Condon effect: Absorption from the lowest vibrational level $v'' = 0$ should give a single maximum, but absorption from each of the levels $v'' = 1, 2 \cdots$ which are considerably populated at room temperature in iodine vapor, must yield two maxima corresponding to the wavefunction maxima at the left and right sides of the potential curve. Whether or not the over-all picture shows two maxima obviously must depend on the relative populations of the v'' levels, and apparently is also affected by pressurization.

As conceivable alternatives to the 1441, $^1\Sigma_u^+\leftarrow X$ interpretation of the Fk Cordes, PR, and KM bands,[55] one may look at other transitions allowed by the case c selection rules. These include the $1_u\leftarrow X$ transitions discussed in the second two paragraphs above, and the following $0_u^+\leftarrow X$ transitions: 2332, $^3\Sigma_u^-(0^+)\leftarrow X$; 2332, $^1\Sigma_u^+\leftarrow X$, and 1342, $^3\Pi_{0^+u}\leftarrow X$. The last one of these may be excluded not only for reasons of too low intensity, but also because its frequency is surely too high (cf. Table I). The transitions to the 2332 states should be relatively weak because the transition from X is a two-electron jump in terms of MO's; however, the transition to the $^1\Sigma_u^+$ state might have considerable intensity but only by stealing it from 1441, $^1\Sigma_u^+\leftarrow X$. Case-c-allowed transitions to 1_u states must be very weak since these must borrow intensity from case a or case b allowed transitions and since even the transition 2341, $^1\Pi_u\leftarrow X$ which is allowed by ordinary selection rules is experimentally observed to be weak. It can be concluded without question that (a) the high observed intensity of the bands peaking at 1825 Å is due to the strongly allowed 1441, $^1\Sigma_u^+\leftarrow X$ transition, but (b) some

or even most of the other transitions just mentioned may also be weakly present hidden under the strong 1441, $^1\Sigma_u^+\leftarrow X$ bands.

The Fk Cordes, PR, and KM bands may then properly be called the $D\leftarrow X$ bands, as they were some time ago. Something must now be said about the fact that some authors, in particular Venkateswarlu,[50] then Mathieson and Rees,[37] have analyzed these bands as two systems, with the Fk Cordes bands attributed to a separate transition $H\leftarrow X$.

Mathieson and Rees argued that there are two systems, because in saturated hydrocarbon solution a shoulder indicative of a second peak at about 2200 Å is superimposed on the strong absorption here called $D\leftarrow X$. But this second peak, which appears *only* in solutions, not in the vapor, has been shown to be a contact charge transfer spectrum resulting from interactions between the iodine and the solvent molecules. (See Ref. 46 and references given there.)

On the other hand, Venkateswarlu's analysis[48] of the Fk Cordes bands as a separate system with ν_c at 51 708 cm^{-1} is unacceptable. All the bands in his Table I, taken from Cordes, can be arranged in *one single* progression, with frequencies given to a fairly good approximation by

$$\nu = 51\,417 + 55.2n - 0.090n^2, \qquad (11)$$

where n is to be interpreted as $v' - x$, v' being the vibrational quantum number in the 1441, $^1\Sigma_u^+$ state, and x is some large number. Nobs and Wieland have arrived at the same conclusion, but have not yet published details.[58] The single progression represented by Eq. (11) must be interpreted as due to bands with $v'' = 0$ for the ground state, which should be the strongest of the observed bands. This interpretation was first proposed by Cordes. Venkateswarlu has arranged the bands in *four* progressions with v'' varying from 0–3, but an examination of his Table II shows definitely unacceptable discrepancies.[63]

That the bands have a 0_u^+ upper state is consistent with, though not assured by, the fact that absorption of an iodine line at 1830.4 Å (see Sec. VII) gives rise to several doublet resonance fluorescence series (P and R branch lines).[64] Verma's analysis[64] also shows some vibrational intervals for the 1441, $^1\Sigma_u^+$ state which are in accord with Eqs. (11) and (12) given below, and gives reasonable B_v values for the vibrational levels involved.

Wieland in a further investigation[59] obtains a formula

$$\nu = 40\,623.9 + 104.165v' - 0.2422465v'^2$$
$$+ 0.453864 \times 10^{-3}v'^3 - 0.70641 \times 10^{-6}v'^4$$
$$+ 6.41845 \times 10^{-10}v'^5 - G''(v'') \quad (12)$$

which fits the uv absorption bands (Cordes, KM, and PM, as remeasured by Nobs and Wieland) in the region λ 1770–2100 Å, with $v' = 98$–259 and $v'' = 0$–7. [$G''(v'')$ is the vibrational energy formula for the ground state,

X.²] However, the v' numbering is based on the fact that Eq. (12) also fits all red-degraded emission bands near λ 3425 attributed to $D\rightarrow X$ transitions from $v'=0$ and other low v' values, but this attribution is inconsistent with an observed isotope effect (see Sec. VIII). Hence, the v' numbering implied by Eq. (12) cannot be considered reliably established. Equation (12) supersedes an earlier analysis by Wieland and Waser,[65] which located ν_{00} of $D\leftarrow X$ at 33 292 cm⁻¹ and which led Nobs and Wieland[58] to conclude that absorption in the Fk Cordes bands of the atomic line 1830.4 Å corresponds to a vibrational quantum number $v'=286\pm3$ of the D state. In terms of Eq. (12), this would be $v'=204$, $v''=0$. It is clear in any event that v' is very much larger than n of Eq. (11).

Consideration must now be given to the 2332, $^3\Sigma_u^-(0^+)$ state which is predicted in Table I to have a vertical energy 0.8 eV less than for the 1441, $^1\Sigma_u^+$ state. The transition 2332, $^3\Sigma_u^-(0^+)\leftrightarrow X$ should be weakly allowed by mixing of the upper state with 1441, $^1\Sigma_u^+$. The predicted position of this transition in absorption, according to Table I, locates its $\nu_{\max}$ approximately at the room-temperature onset of the $D\leftarrow X$ bands. It may well be that its bands are weakly present among the bands at the long wavelength end of the Cordes bands near 2000 Å; or, since the predictions of Table I are not exact, they may be hidden under the Cordes bands.

In connection with the question of the dissociation products of the 1441, $^1\Sigma_u^+$ state, we may note[54,58] that Birge–Sponer extrapolation to convergence of the frequencies of the Fk Cordes bands as given by Eq. (11) gives an energy of only about 60 000 cm⁻¹, whereas the dissociation asymptote shown in Fig. 1 $(^3P_0+{}^1S)$ lies at 76 522 cm⁻¹, and the lowest *possible* dissociation asymptote, $\cdots 5p^46s$, $^4P_{5/2}$ plus $\cdots 5p^5$, $^2P_{3/2}$, lies at 66 093 cm⁻¹. The discrepancy is attributable to the fact that the vibrational levels of an ion-pair state cannot be extrapolated in the Birge–Sponer manner but go to much higher energies.[66] The difficulty is overcome when an equation like Eq. (12) is used.

The foregoing discussion leaves no firm basis for drawing the D state potential curve in Fig. 1. However, evidence presented in Secs. VII and VIII leads to a value of roughly 41 000 cm⁻¹ for ν_e of this state. Figure 1 has been drawn accordingly. In any event, 1441, $^1\Sigma_u^+$ tends to go to $I^+(^3P_0)+I^-(^1S)$ according to the case c noncrossing rule.

In the spectrum of iodine at higher temperatures and pressures, Skorko[67] found a strong apparently continuous absorption region extending for a short distance toward higher frequencies from a rather sharp long-wavelength edge at λ 3427 and a similar but weaker region with long-wavelength edge at λ 3263. In a 26-cm long quartz tube, the λ 3427 region was first seen at 775°C at a pressure of 80 mm Hg, the λ 3263 region at 885°C and 760 mm, or at 150 mm at 1050°C. At 1050°C a long series of narrow diffuse bands extending from

λ 3427 up to 2974 Å was also seen. Warren[57] reported results similar to those of Skorko (see Fig. 2 of his paper for a photometer tracing). In recent work by Wieland[68] the narrow diffuse bands at 1130°C are seen extending with increasing intensity toward still shorter wavelengths, merging doubtless into the KR, PM bands. On the other hand, the narrow diffuse bands are probably associated in part also with the apparent continua with edges at λ 3427 and λ 3263; under high resolution only narrow bands are seen throughout the regions from λ 3427 to shorter wavelengths.[68] The most likely interpretation appears to be that the narrow bands include $D\leftarrow X$ bands arising from high v values of state X, but *also* include closely packed absorption bands of two additional electronic transitions.

Referring to Fig. 1, it is seen that at high temperatures not only the high vibrational levels of state X but also the vibrational levels of the 2431, $^3\Pi_{2u}$ and $^3\Pi_{1u}$ states must begin to be populated. Absorption transitions from these two levels to the respective predicted ion-pair levels 1432, $^3\Pi_{2g}$ and $^3\Pi_{1g}$ (see Table I) are expected with *high intrinsic intensity* since the MO transition $\sigma_u5p\leftarrow\sigma_g5p$ is exactly the same as for the $D\leftarrow X$ bands.[69] As compared with equal-energy high-v levels of state X, $^3\Pi_{2u}$ and $^3\Pi_{1u}$ have the advantage of a double statistical weight; however, Franck–Condon considerations may be more important in accounting for the conspicuousness of the two absorption regions with edges at λ 3427 and λ 3263.

We now assume that the regions λ 3427 and λ 3263 can be identified with absorptions respectively from the $^3\Pi_{2u}$ and $^3\Pi_{1u}$ states. The Boltzmann factors $e^{-E/kT}$ for the temperatures at which the λ 3427 and λ 3263 groups first become visible are then approximately as follows, using $E\approx1.25$ eV for $^3\Pi_{2u}$ and $E\approx1.46$ eV for $^3\Pi_{1u}$ from Fig. 1: $e^{-E/kT}=0.98\times10^{-6}$ for $^3\Pi_{2u}$ (775°C, 80 mm), 1.0×10^{-6} for $^3\Pi_{1u}$ at 885° (760 mm), and 5.5×10^{-6} at 1050° (150 mm). After allowing for the pressure differences, it appears that the $^3\Pi_{1g}\leftarrow{}^3\Pi_{1u}$ absorption is about one-tenth as strong as the $^3\Pi_{2g}\leftarrow{}^3\Pi_{2u}$ absorption. Theoretically the two electronic transitions should be about equally strong, but differences in Franck–Condon factors and the fact that the $^3\Pi_{1u}$ state probably has only one-half or one-third as many vibrational levels as the $^3\Pi_{2u}$ state, also perhaps a difference in $D\leftarrow X$ background, may plausibly account for the higher apparent over-all intensity of the $^3\Pi_{2g}\leftarrow{}^3\Pi_{2u}$ transition.

By the same token, the absorption transition $^3\Pi_0{}^+_g\leftarrow{}^3\Pi_0{}^+_u$ is predicted with an electronic transition moment about the same as for $^3\Pi_{2g}\leftarrow{}^3\Pi_{2u}$ and $^3\Pi_{1g}\leftarrow{}^3\Pi_{1u}$. Now the firmly authenticated emission band system $E\rightarrow B$ (see Sec. VIII) can probably be identified as 1432, $^3\Pi_0{}^+_g\rightarrow2431$, $^3\Pi_0{}^+_u$ in emission. For this system,[68] $\nu_{00}=$ 25 630.5, which corresponds to λ 3880. But in Wieland's 1130°C absorption spectra at 760 mm[68] which show the Skorko groups λ 3263 and λ 3427, there are no indications of bands in this region, although at 1130°C, $e^{-E/kT}$

for the B, $^3\Pi_{0^+u}$ state is 1.14×10^{-7}. One can perhaps conclude that the E←B bands, which (whatever they are) *must* occur in absorption at high temperatures, are weaker than one would expect if they are $^3\Pi_{0^+g}$←$^3\Pi_{0^+u}$. In case Verma's interpretation of the emission bands with low-frequency edge at about λ 3460 (see Sec. VIII) should be at least partially correct, *the latter* are, or include, $^3\Pi_{0^+g}$→$^3\Pi_{0^+u}$, and the presumably corresponding λ 3427 absorption bands would then be, or would *include*, the $^3\Pi_{0^+g}$←$^3\Pi_{0^+u}$ absorption.

The related transitions $^1\Pi_g$–$^1\Pi_u$ and $^3\Pi_{0^-g}$–$^3\Pi_{0^-u}$ of the same upper and lower electron configurations are not expected to be found in absorption since $^1\Pi_u$ and $^3\Pi_{0^-u}$ states correspond to repulsion curves (Fig. 1 and Sec. V). However, they should occur in emission as continuous spectra; their upper states should have stable ion-pair potential curves (see Sec. VIII).

The locations of the ion-pair levels of the configuration 1432 just discussed will be further considered in Sec. VIII in connection with a discussion of the iodine emission spectrum. Of special interest is an examination of a very strong emission region which looks like the absorption region with low-frequency edge at λ 3427, but which differs from the latter in that its edge is at about λ 3460. This puzzling emission region also perhaps contains evidence on the low v' levels of the D state.

VII. THE EMISSION SPECTRUM OF IODINE VAPOR IN THE ABSENCE OF FOREIGN GASES; THE D→X FLUORESCENCE SPECTRUM

Numerous reports have been published on the emission spectrum of iodine, lying in the blue, violet, and ultraviolet. The spectrum can be excited (a) by absorption of ultraviolet atomic lines (resonance and fluorescence spectra) either in iodine vapor alone[70–73] or in iodine vapor plus foreign gases[74–76], (b) by electrical discharges either in iodine vapor alone[56,77–80,64] or in iodine vapor plus foreign gases[81,65,82,83], or (c) by iodine vapor in active nitrogen.[84,76]

In the absence of foreign gases the spectrum consists in one or more typical resonance series at short wavelengths, followed at longer wavelengths by groups of diffuse bands. For example, Oldenberg showed that the tin line at λ 1900 gives rise to a long series of resonance lines of nearly uniform intensity (but alternate lines somewhat stronger) extending from λ 1900[85] to λ 2173, followed at longer wavelengths[86] as far as λ 4800 by the diffuse bands which were first reported by McLennan.[70,87] Other atomic lines give rise to other resonance series.[70–72] The fact[77,78,64] that resonance series are generated in electrical discharges as well as by absorption of atomic lines of various elements was explained by Kimura and Tonomura,[77] and by Asagoe,[78] as an example of "autoresonance," in which iodine atomic lines excited by the discharge are absorbed by iodine molecules, giving rise to the resonance series. By far the most conspicuous resonance series[78,64] so ob-

tained is that excited by the iodine atom line λ 1830.4. Each resonance series consists of doublets, showing that the initial state is a single vibration–rotation level of an electronic state which is undoubtedly the $D(1441, ^1\Sigma_u^+)$ state, while the final levels are vibration–rotation levels of the ground state[77,78,64] and (a few) of a state which may be 2341, $^3\Pi_{0^+g}$ or 2422, $^3\Sigma_g^-(0^+)$—see Sec. III.

McLennan reported that the spectrum of diffuse bands is independent of the exciting atom line or lines and of temperature, but Duschinsky and Pringsheim[73] showed that, although the general appearance is unchanged, there are small systematic shifts in the diffuse bands; this important result will be discussed below. For the most part, reported lists of wavelengths of the diffuse bands by different observers[70,71,79,80,88] agree well. Some report a few more bands, perhaps because of the use of a more sensitive photographic plate. Oldenberg[71] lists some bands between 3338 and 3442 Å which are not given by others. In general, it appears that the spectra excited by atomic lines and by mild electrical discharges are very similar. However, it appears that to some extent there is *additional* excitation by electrical discharges (see especially Asagoe and Inuzuka[79]).

Another significant fact about the diffuse bands must now be noted. Curtis and Evans[56] have published a photograph and microphotometer tracings which show that at sufficiently low pressures (0.001 torr), using electrical excitation, the diffuse bands reach a climax with a group near 3250 Å, then drop to low intensities at wavelengths greater than 3300 A, while at higher pressures (0.16 torr) there are additional groups of strong diffuse bands at wavelengths up to 4800 Å. These additional bands are also present, but much weaker, at 0.001 torr. At shorter wavelengths, a continuous background develops underlying the diffuse bands at the higher pressure. The following conclusions seem justified: (1) The primary process in which the resonance series and diffuse bands are excited gives diffuse bands which extend from the farther ultraviolet only to and including the group near 3250 Å; (2) at higher pressures collisions transfer excited molecules to other electronic states that give rise to additional diffuse bands, especially at longer wavelengths. Most probably the initial excitation is mainly transition to a high energy vibration–rotation level of the D state through absorption of the iodine atom λ 1830.4 line. The fact that most observers report diffuse bands extending to λ 4800 may be ascribed to their use of pressures of iodine vapor high enough to cause collisional transfer to other than the initially excited electronic state. [Note that the vapor pressure of iodine at (1933 British) room temperature is 0.16 torr, at which pressure Curtis and Evans observed the complete set of diffuse bands.] That collisional transfer to other electronic states can readily occur is reasonable when one notes the large number of predicted ion-pair states in Fig. 1, whose potential curves (all with broad minima mostly not shown, because of crowding) must each be associated with

numerous vibrational levels, so that the vibrational levels of the D state are embedded in a rather densely packed mass of levels belonging to other electronic states. It must apparently be concluded that electronic transfer takes place more readily than vibrational transfer.

To summarize: It seems reasonably clear that (1) the spectrum excited in iodine vapor at very low pressures, whether by mild electrical discharges or by absorption of foreign atomic lines, is a fluorescence spectrum arising from a high vibrational level or levels of the D state and including one or more doublet resonance series whose continuation at longer wavelengths is a series of diffuse bands culminating in a relatively strong group near λ 3200; (2) at higher pressures, collisional transfer to high vibrational levels of other electronic states gives rise to additional diffuse bands all or mostly at longer wavelengths. Let us refer to (1) and (2), respectively, as the *primary* fluorescence spectrum and the *secondary* fluorescence spectrum.

Concerning the nature of the diffuse bands, it has been suggested[80] that they are "fluctuation bands"[89] in which the final electronic state is one with a repulsive potential curve, of which there are many (see Fig. 1). As will be seen below, this suggestion is probably correct for the secondary, but not for the primary diffuse bands. The diffuse bands are broad (more than 100 cm^{-1} wide) and symmetrical: See Refs. 73, 79 and 76 for very instructive microphotometer traces.

Venkateswarlu[80] has sought to explain the diffuse bands in terms of transitions from two or more vibrational levels of five different electronic states to a large number of different repulsive states, but his detailed assignments are very unconvincing. No other, satisfactory, explanation of the diffuse bands has been given hitherto. A new explanation of the primary series of diffuse bands which appears convincing will now be offered, based on a theoretical treatment in an accompanying paper.[90] Let us call this paper FC.

In Fig. 3 of FC two potential curves are shown of which the lower, $U''(R)$, has been drawn to conform to that of state X of iodine, while the upper is a simple-harmonic-oscillator curve which may be taken as an extremely crude approximation to the potential curve $U'(R)$ of the D state. Spectroscopic transitions are considered from an initial state of energy E' down to a series of lower states E'', partly discrete (for $E'' < D_X$), partly continuous ($E'' > D_X$); their frequencies are given by $\nu = (E' - E'')/h = W/h$; E' is the energy of a particular vibration–rotation level of state D, from which transitions occur with the selection rule $\Delta J = \pm 1$ down to the levels of state X. D_X is the dissociation energy of state X. The frequencies for $E'' < D_X$ correspond to the observed resonance series, those for $E'' > D_X$ are to be identified with the diffuse bands (cf. Fig. 6 of FC). $E''(R)$ in Fig. 3 of FC is a curve determined classically by the Franck principle but by means of which the relative probabilities of transitions

to various values of E'' are determined (see FC). It is seen that $E''(R)$ has a maximum value lying in the continuum of state X. To this maximum of E'' corresponds a minimum frequency $\nu_{\min}$, but a maximum of intensity, in the roster of the diffuse bands. This predicted region of high intensity at the long-wavelength end of the diffuse bands can now be identified with the observed strong group of diffuse bands near λ 3250.

The observed group consists of a series of about half a dozen bands spaced at regular intervals. The interval between bands will be called the "fluctuation interval." Duschinsky and Pringsheim[73] studied the spectrum as excited in fluorescence by a variety of exciting lines; different exciting lines would lead to different vibrational levels of state D, hence different values of E'. They found (see their Table II) that, although the position of maximum intensity in the λ 3250 group shifts only slightly with E', the pattern of bands is considerably modified and, in particular, the fluctuation interval $\delta\nu$ is considerably smaller for smaller E'.[91] Thus, for excitation by wavelengths less than 1900 (probably mainly the iodine atomic line λ 1830.4), $\delta\nu = 224$ cm^{-1}, for the Zn line λ 2139, $\delta\nu = 196$, for the Hg line λ 2537, $\delta\nu = 165$. Now theoretically,[92] for $\delta\nu$ near $\nu = \nu_{\min}$,

$$\delta\nu = \frac{[2(E' - E_0 - \delta)/\mu]^{1/2}}{2L^*}, \qquad (13)$$

where E_0 is the energy of the D state at the bottom of its potential curve, δ is approximately equal to $\frac{1}{2}kx_m^2$ where k is the harmonic force constant for small vibrations in the D state and x_m is the value of x corresponding to the maximum of the $E''(x)$ curve in Fig. 3 of FC, and μ is the reduced mass of I_2 (63.5 m.u.). L^* is an effective length somewhat smaller (see FC) than the distance, taken at an energy $E' - h\nu_{\min}$, between $x_{\min}$ and the value of x at the small R turning point of the state X potential curve.

Now, although E_0, x_m, and δ are not known, they can be estimated sufficiently well from $h\nu_{\min}$ so that Eq. (13) can be used to calculate a good value of L^* from the observed $\delta\nu$. If excitation is by λ 1830.4, E' is about 54 600 cm^{-1}. Then (see below) if R_e for the D state is 3.6 Å, E_0 is about 41 200 cm^{-1}, δ is about 420 cm^{-1}, and $L^* = 1.77$ Å. If R_e is 4.1 Å, E_0 is about 42 000 cm^{-1}, δ is 2 cm^{-1}, and $L^* = 1.79$ Å. As will be seen below, the combination of $L^* = 1.79$ Å and $R_e = 4.1$ Å is very reasonable.

This result affords strong confirmation of the interpretation given here for the λ 3250 group as a region of maximum intensity forming the long-wavelength end of a fluorescence spectrum. The fact that the position of the maximum of the λ 3250 group is almost independent of the exciting line represents another confirmation of the interpretation. Further, the fact that $\delta\nu$ gets smaller when E' is smaller is in agreement with Eq. (13)[93]; although we do not have exact values of E'

and L^*, the order of magnitude of the change in $\delta\nu$ with E' is entirely reasonable.

From the data now available it is possible to obtain an approximate value of the energy E_0 of the D state at the bottom of its potential curve $U'(R)$. Namely one sees from Fig. 3 of FC that

$$E_0 = h\nu_{\min} + (D_X - \Delta) - \delta, \qquad (14)$$

where the quantities Δ and δ, taken at the R value, say R_m, where $E''(R)$ has its maximum, are indicated in Fig. 3 of FC. Now R_m is not known, although we would like to know it. However, it is related to the equilibrium internuclear distance R_e for state D in the following way. $E''(R)$ is so constructed that $E'' = U'' + K$, where K is the kinetic energy associated with the $U'(R)$ curve. Now E'' is a maximum when

$$dE''/dR = dU''/dR + dK/dR = 0,$$

hence when $dU''/dR = -dK/dR = dU'/dR = k(R - R_e)$ since $U' \approx \frac{1}{2}k(R - R_e)^2$ in the neighborhood of R_e.[94] Hence

$$\delta = \frac{1}{2}k(R_m - R_e)^2 = \frac{[dU''/dR]^2}{2k}, \qquad (15)$$

where $k = 4\pi^2 c^2 \mu \omega_e^2$. Since $U''(R)$ is known,[2] dU''/dR and from it δ and therefore also $R_m - R_e$ are known, provided ω_e for the D state is known. Actually an exact value of ω_e is not known but a value of 100 cm^{-1} was assumed [cf. Eq. (12)]; exactness here is not important since δ is not very large. Since Δ, hence $D_X - \Delta$, is known as a function of R,[2] a value of E_0 can now be computed by Eq. (14) for any trial value of R_m; the corresponding value of R_e is also known, from the second equality in Eq. (15). Calculations were made for several R_e values.

The following shows the results obtained:

$R_e(\text{Å})$	3.2	3.3	3.4	3.5	3.6	4.1
R_m	3.57	3.63	3.69	3.76	3.81	4.115
δ	1370	1040	780	590	420	2
Δ	3040	2660	2320	1970	1970	864
$E_0(\text{cm}^{-1}\times 10^{-3})$	38.9	39.7	40.3	40.8	41.2	42.4

Since R_e is not likely to be far outside the range tried, we conclude that E_0 is not far from 41 000 cm^{-1}. As evidence concerning the value of R_m, hence of R_e and of E, consideration can be given to the values of L^* derived above (1.77 Å if $R_e = 3.6$ Å, 1.79 Å if $R_e = 4.1$ A). L^* should be a quantity somewhat smaller than $R_m - 2.2$, 2.2 Å being the value of R at which U''' is equal to $E''(R_m)$. On this basis, $R_e = 4.1$ Å, which gives $R_m - 2.2 = 1.92$ Å, seems a good estimate, while $R_e = 3.6$ Å, with $R_m - 2.2 = 1.61$ Å seems to be too small. While this conclusion is not certain, in view of some of the assumptions involved, there are other indications which point toward a relatively large R_e value for state D. For example, in the case of H_2, the ratio of the R_e values of the states analogous to D and X of I_2 is $1.289/0.742 = 1.735$; if the same ratio held for I_2, R_e of state D would be $2.666 \times 1.735 = 4.63$ Å. More closely relevant, work on an excited state of Cl_2[95] which is probably analogous to 1432, $^3\Pi_0{}^+{}_g$, of I_2, an ion-pair type of state, gives an R_e ratio of 1.363 to R_e of state X; if the same ratio held for I_2, R_e would be 3.64 Å. In view of the fact that different ion-pair states should be similar in R_e but not identical, the value of about 4.1 Å deduced above for state D of I_2 is not unreasonable.

If R_e of state D is 4.1 Å, the table above gives E_0 about 42 400 cm^{-1}. However, the correct E_0 should be somewhat smaller. The observed position of $\nu_{\min}$ should correspond to a maximum value, as a function of χ'', of the Condon integral $\int \chi'(R)\chi''(R)dR$, rather than being given by a matching of de Broglie wavelengths at an energy, hence χ'', corresponding to the semiclassical Franck principle. A review of all the evidence near the end of Sec. VIII leads to E_0 about 41 000 and R_e about 3.8 Å as plausible.

It has now been shown that theory and experiment agree in interpreting the λ 3250 group as the long-wave terminus of the diffuse-banded part of the primary fluorescence spectrum. The long series of diffuse bands observed at shorter wavelengths (see, e.g., Fig. 1 of Oldenberg's 1923 paper[71]) ends theoretically when $E'' = D_X$, being followed at shorter wavelengths by the resonance series. The general characteristics of this series of diffuse bands (somewhat irregularly varying $\delta\nu$ and intensities) appear to be in agreement with the theory, but no attempt at a detailed comparison will be made here. For $\delta\nu$, the theory [cf. Eq. (23) of FC] gives

$$\delta\nu = \frac{(2K''/\mu)^{1/2}}{2L^*}. \qquad (16)$$

K'' here is equal to K' according to the Franck principle; K' is equal to $E' - E_0 - \delta$ of Eq. (13).

The diffuse bands in the fluorescence spectrum at higher frequencies than $\nu_{\min}$ correspond in Fig. 3 of FC

to classical transitions at values of R less than and greater than R_m, and to values of $K''(R)$ less than for $\nu_{\min}$. At the same time L^* changes, with the result that $\delta\nu$ should perhaps increase, then decrease, as ν increases. It should be noticed that except at $\nu_{\min}$, L^* has two values, corresponding to two points on the $E''(R)$ curve which have the same value of E''. Correspondingly, in this ν region there are two contributions, with different $\Delta\nu$, to the intensity at any ν. However, the contribution corresponding to the smaller L^* should be the principal one since the intensity depends not only on $(\int \chi'\chi''dR)$ but also on Q_{el} [see Eq. (2) of FC], and Q_{el} probably falls off strongly at large R. For Q_{el} is proportional to SR for large R, where S is the overlap integral between the X and D electronic wavefunctions,[42] and S falls off rapidly at large R. As has been noted already, the observed diffuse fluorescence bands are nearly but not quite independent of the exciting wavelength, hence of E'. As can be seen by a study of Fig. 3 of FC, this result is expected from the theory not only at $\nu_{\min}$ but also at higher frequencies, except that the point where the diffuse bands stop and the resonance series begins must shift toward lower frequencies as E' increases. No experimental study of the region of the boundary between the resonance series and the diffuse bands has been made. Such an examination, and a detailed study of the diffuse bands lying between the intense group near $\nu_{\min}$ and the end of the resonance series would be of much interest, but will not be attempted here.

However, attention should be called to the fact, not explained here, that the diffuse bands at shorter wavelengths than the compact λ 3250 group show a much coarser spacing than the $\delta\nu$ *within* the λ 3250 group (see reproductions in the references cited above). This coarser spacing may perhaps reflect an additional periodicity in the diffraction pattern represented by the diffuse bands and deserves further theoretical consideration. More satisfactory than the semiclassical treatment used here would be a systematic evaluation of the Franck–Condon integral for the case considered here. Such a systematic evaluation is rendered more difficult by uncertainty as to the form and location of the $U(R)$ curve of the D state. That the diffuse bands at higher frequencies than the λ 3250 group are weaker than the latter is in accord with the theory in FC (see Fig. 6 there). Their lack of complete regularity might be explained in part by an overlapping of bands corresponding to classical transitions for $R > R_m$ and $R < R_m$.

The secondary diffuse bands, those extending from λ 3300 to λ 4800, will now be considered. As has been stated already, these bands can be attributed to transitions from several bound upper electronic states of ion-pair character (cf. Sec. VIII), reached by collisions from molecules initially in the D state, to a variety of repulsive lower states. The general appearance of the spectrum for such a transition can be predicted. The most intense part (see Fig. 5 in FC) should be bounded by two limits, $\nu_{\min}$ and ν_{med}, where $\nu_{\min}$ is determined by the maximum of $E''(R)$, and $h\nu_{\text{med}}$ is given by the difference in energy between the small R classical turning points of the potential curves of the upper (bound) and lower (repulsive) states—see Fig. 2 of FC. At higher frequencies the spectrum should extend with lower intensity as far as $(E' - D_X)/h$. The observed bands conform to these specifications if we assume that the weak higher-frequency parts of these spectra account for the weak continuous background which extends throughout the region of the primary diffuse bands when the iodine pressure is not extremely low. Particularly conspicuous in the observed spectra[56] are groups with long-wave limits near λ 4800, λ 4300, and λ 4150, and (especially intense) λ 3460. Except for λ 3460 no attempt at a detailed interpretation will be made here, although, of course, it would be desirable to obtain an interpretation compatible with Table I and Fig. 1, or modifications of these.

VIII. THE EMISSION SPECTRUM IN THE PRESENCE OF FOREIGN GASES; THE ION-PAIR STATES[96]

Elliott[97] found that when iodine is excited by absorption of Al spark lines λ 1854 and 1862 in a predominant atmosphere of nitrogen, the diffuse bands become faint and are replaced by some well-defined, red-degraded systems of sharp bands: 4420–4000 Å(E), 2730–2486 Å(F), and 3460–3015.[76,97] Waser and Wieland,[65] and later Venkateswarlu,[82] and then Verma,[83] obtained the same bands using a high-frequency discharge with iodine in a predominant atmosphere of argon; Venkateswarlu and Verma also found a much weaker system in the region 2785–2731 Å.

Strongest are the λ 3460–3015 bands. In these bands the intensity falls off steadily toward shorter wavelengths from a maximum near λ 3425. This emission region may very likely be related to the absorption region with long-wavelength limit at λ 3427 (see Sec. VI), but differs from the latter in that its long-wavelength edge is at about λ 3460, and also in its much greater extension toward short wavelengths. At very low pressures of iodine, without foreign gases, the λ 3425 emission band is absent or nearly so according to a photograph by Curtis and Evans[56] (see Sec. VII) and is very weak in the presence of nitrogen at low pressures according to Elliott.[76] At higher pressures of pure iodine,[56] or iodine plus nitrogen at up to a few centimeters pressure,[76] the λ 3425 region appears continuous or with only faint indications of banded structure, while at higher pressures of foreign gas (nitrogen,[76] with fluorescent excitation, or argon[81–83] with mild electrical excitation) the structure consists at least mainly of a great number of red-degraded bands. Whether at low pressures the structure involves a true continuum is not clear; perhaps the apparent continuum may be the result of a superposition of densely packed bands. On the other hand, it seems possible that

a true continuum forming part of the secondary diffuse spectrum may by chance occur in this same wavelength region. Or a continuum due to the transition 1432, $^1\Pi_g \to 2431$, $^1\Pi_u$ or 1432, $^3\Pi_{0^-g} \to 2431$, $^3\Pi_{0^-u}$, ending in a repulsive curve (see Fig. 1) might be present.

The vibrational analysis of the $\lambda 3425$ emission bands has proved a difficult and uncertain task. Elliott[76] gave an analysis with $\nu_e = 33744$ and $\omega_e' = 104$ cm^{-1}, attributing the bands to the D$\to$X transition with low values of v'. These low v values would have been reached by collisions with N_2 molecules following initial excitation to a very high vibrational level of the D state. Wieland and Waser[65] gave a slightly different analysis with $\nu_e = 33347$. However, their analysis did not include the shorter-wavelength bands (below $\lambda 3237$), and they suggested that these might belong to a different system.

Somewhat earlier, Venkateswarlu[82] gave an analysis with $\nu_0 = 39131$ and $\omega_0' = 103.0$ corresponding to a considerably different vibrational numbering in the X state; his analysis included all the bands. Subsequently Verma,[83] working in Venkateswarlu's laboratory, gave a radically different analysis in which the lower state of the transition is the B $^3\Pi_{0^+u}$ state; the altogether most probable upper state would then be 1432, $^3\Pi_{0^+g}$ (see the reasoning in Sec. VI). Verma's analysis has the advantage over Venkateswarlu's of making much better sense in terms of the Franck–Condon principle.

In 1968, Tellinghuisen investigated the $\lambda 3425$ bands using two isotopes of iodine (natural ^{127}I and radioactive ^{129}I), while at the same time and place (Berkeley) Wieland examined the bands of the natural isotope under high resolution.[59] Equation (12) which Wieland has fitted to the Fk Cordes and PR and KM D$\leftarrow$X bands, also fits very well the $\lambda 3425$ bands (in so far as they are red degraded) of the natural isotope if they are assumed to be D$\to$X bands and if a very probable v' assignment ($v' = 0$–18) and a reasonable assignment of the v'' values ($v'' = 60$–80) of state X are made. Unfortunately, the isotope effect does not fit at all, although for two other transitions (F$\to$X and E$\to$B, —see below) the isotope shift agrees excellently with theoretical expectation.

Tellinghuisen's tentative conclusion[98] is that the final state of the $\lambda 3425$ bands is the 2431, $^3\Pi_{2u}$ state. The isotope shift (about 7 cm^{-1} for the strongest bands, near $\lambda 3427$, to which Wieland and Tellinghuisen assign $v' = 0$) would become zero for bands at just about the expected position of the $v'' = 0$ level of the $^3\Pi_{2u}$ state (at about 1.25 eV, see Fig. 1 and Sec. VI). The upper level of the bands would then be the ion-pair state 1432, $^3\Pi_{2g}$ (see Sec. VI), and the near coincidence of the emission bands whose low-frequency edge is at $\lambda 3460$ with the high-temperature absorption bands with low-frequency edge at $\lambda 3427$ would be understood. The difference in position of the low-frequency edge could perhaps be explained on Franck–Condon grounds. Wieland[59] finds that for the interpretation of the $\lambda 3425$

bands of $^{127}I_2$ as $^3\Pi_{2g} \to {}^3\Pi_{2u}$, the following equation fits:

$$\nu = 30\,348.35 + (104.19v' - 0.245v'^2 + 0.000470v'^3)$$
$$- (109.003v'' - 1.3655v''^2 - 0.0034513v''^3). \quad (17)$$

Here the upper-state vibrational expression is equivalent to that of Eq. (12). A corresponding equation fits the $^{129}I_2$ bands.

It should be kept in mind that the high-temperature absorption spectrum includes not only the strong narrow region near $\lambda 3427$ (and a weaker one near $\lambda 3263$) but also, at the highest temperatures studied, an extensive series of weaker bands which almost certainly are D$\leftarrow$X bands forming an extension of the PR, KM bands (see Sec. VI). In this connection it is significant that, besides the red-shaded bands reported by Elliott in fluorescence and by others under mild electrical excitation, Wieland[59] finds that under stronger electrical excitation many "linelike bands" appear (Wieland's "Spectrum II"), which otherwise (Spectrum I) are no more than weakly present. Further,[59] the linelike bands agree extensively with absorption bands. Although the picture is still unclear, it seems likely that both D$\to$X and $^3\Pi_{2g} \to {}^3\Pi_{2u}$ bands are present in the $\lambda 3425$ region, in both cases with a preponderance of low v' values attributable to collisional degradation.

A further possibility is that Verma's analysis of the $\lambda 3425$ bands, already mentioned, is correct, or partially so. In its favor is the fact that it makes good sense in terms of the Franck–Condon principle, also that it predicts an isotope effect which seems to be in agreement with what is observed. Thus, for example, the band at $\nu = 29\,320$ which Verma classifies as 0, 8 has an isotope shift[68] of 7 cm^{-1} in exact agreement with the theoretical value (7.2 cm^{-1}) for a 0,8 band of a transition ending on the B $^3\Pi_{0^+u}$ state. However, the agreement may be accidental since the analysis as $^3\Pi_{2g} \to {}^3\Pi_{2u}$ can also account (exactly) for the isotope effect. The v' assignments in Verma's analysis, ranging up to $v' = 36$, seem somewhat improbable. Wieland, in correspondence with the writer, after a careful study states that "Verma's 1958 analysis is certainly wrong as far as the red-degraded bands are concerned." This leaves open the interpretation of the linelike bands of Wieland's Spectrum II.

Before going further with the discussion of the $\lambda 3425$ bands, let us consider some of the other bands which are brought out by foreign gases. Fairly strong are the E bands (4420–4000 Å) to whose analysis as ending on the 2431, $^3\Pi_{0^+u}(B)$ state everyone[81–83] agrees and of whose correctness the isotope effect as studied by Tellinghuisen and Wieland gives definite assurance.[59] The intensity distribution[82] shows a Franck–Condon parabola consistent with this assignment from which it is possible to estimate that R_e for the upper state is about 3.55 Å. The E upper state is a typical ion-pair state with $\omega_e = 101.59$, $x_e\omega_e = 0.238$, and $\nu_e = 41\,411$

cm^{-1}.[68] This ν_e is very near to that of the D state as estimated in Sec. VII. Waser and Wieland proposed that the E state is $^3\Pi_g$ (doubtless 1432, $^3\Pi_0^+{}_g$). This assignment is very probable unless Verma's analysis of the λ 3425 bands as ending on the $^3\Pi_0^+{}_u(B)$ state is correct, in which case $^3\Pi_0^+{}_g$ is almost certainly the upper electronic state of the latter bands, or some of them.

In that event, the most probable assignment for the E state is 2242, $^1\Sigma_g^+$. However, it is then necessary to assume strong case-c mixing between the two pure states 1432, $^3\Pi_0^+{}_g$ and 2242, $^1\Sigma_g^+$. The intensity of the $E\rightarrow B$ bands would then be ascribed to stealing of intensity from the $^3\Pi_0^+{}_g\rightarrow B$ bands. According to the case c noncrossing rule and assuming that the energy order given in Table I for the vertical energies is correct, the E state should then tend to dissociate to $I^+(^3P_0)+I^-(^1S)$ and the upper state of the λ 3450–3015 bands to $I^+(^1D)+I^-(^1S)$.[99] However, as discussed in the next-to-last paragraph of Sec. III, formally singlet and triplet states of the molecule should have a strong tendency to dissociate, respectively, to give formally singlet and triplet state of I^+; but note that because of strong spin-orbit coupling in I^+, its low $^3P_0$ and $^3P_2$ states are considerably mixed with ^1S and ^1D, respectively.[100] At small R values, then, state E would be predominantly 2242, $^1\Sigma_g^+$ but partly 1432, $^3\Pi_0^+{}_g$, while at large R values it would be predominantly 1432, $^3\Pi_0^+{}_g$ and partly 2242, $^1\Sigma_g^+$. For the upper state of the λ 3425 bands converse relations would hold. In terms of *pure* singlet and triplet states, the $U(R)$ curves of the two states would then be regarded as the resultants of an avoided crossing. However, the correctness of this elaborate explanation seems rather unplausible, and the need for it can be taken as an argument against Verma's analysis of the λ 3425 bands. On the other hand, the fact that $E\leftarrow B$ absorption bands have not been observed at high temperatures (see near end of Sec. VI) argues against the identification of the E state as the upper state of a strongly allowed $^3\Pi_0^+{}_g\leftarrow{}^3\Pi_0^+{}_u$ transition, and thus in favor of a $^1\Sigma_g^+$ identification and of Verma's analysis.

All investigations[65,81–83] are in agreement on the interpretation of the $F\rightarrow X$ bands as ending on state X, and in particular the isotope effect as studied by Tellinghuisen[59] gives assurance of its correctness. Also, the Franck–Condon parabola agrees with this interpretation. From the form of this parabola it is possible to estimate that R_e for the upper state is about 3.6 Å. The F state is a typical ion-pair state with $\nu_e=47\,218$, $\omega_e=95.96$ cm^{-1}, $x_e\omega_e=0.3623$ cm^{-1}.[68,81,83] In the writer's opinion it is most probably the 2332, $^1\Sigma_u^+$ state. The very appreciable intensity of the $F\rightarrow X$ transition may be explained as acquired from the $D\rightarrow X$ transition as a result of configuration interaction between the D and F states.

The very weak system in the region 2785–2712 Å was found by Venkateswarlu[83] and extended by Verma.[83] Although it can be analyzed[82] as ending on state X, its

TABLE IV. Vertical (T_v) and minimum (T_e) energies of several states of I_2 (in cm^{-1}).

State	T_v	T_e	T_v-T_e
2332, $^1\Sigma_u^+(F)$	64 700[a]	47 207[d]	17 500
1432, $^3\Pi_{1g}$	60 700[a]	42 300[e]	18 400
1441, $^1\Sigma_u^+(D)$	54 600[b]	41 000[f]	13 600
1432, $^3\Pi_0^+{}_g$	65 600[a]	{41 411[g] (or) / 45 937[h]}	{24 200 / 19 700}
2242, $^1\Sigma_g^+$	61 500[a]	(41 411 if)[i]	19 600
1432, $^3\Pi_{2g}$	60 000[a]	40 300[e]	19 700
2431, $^3\Pi_0^+{}_u(B)$	18 800[c]	15 771[j]	3 000
2431, $^3\Pi_{1u}(A)$	15 000[c]	11 888[j]	3 100
2431, $^3\Pi_{2u}$	13 500[c]	10 100[b]	3.400

[a] Estimates from Table I (and see Fig. 1).
[b] Fairly accurate, observed or probably observed (see Sec. VI).
[c] Fairly accurate (see Sec. V).
[d] Accurate value (see this section for probable identification of F state).
[e] Based on Absorption Spectrum (Sec. VI); see this section.
[f] See Sec. VII and near the end of this section.
[g] Accurate value if E level is 1432, $^3\Pi_0^+{}_g$ (see this section).
[h] Accurate value if Verma's analysis of λ 3425 bands is correct (see this section).
[i] Accurate value if Verma's analysis of λ 3425 bands is correct, and if this is the E level.
[j] Accurate, see Ref. 3.

intensity distribution suggests[83] that it ends on the B state. From the form of the Franck–Condon parabola, an approximate R_e value for the upper state is 3.0 Å; from Verma's analysis, $\nu_e=51\,847$, $\omega_e=112.4$, $x_e\omega_e=0.71$. The writer has not found any reasonable assignment for this state as one of the ion-pair states of Table I, either on the basis of Verma's analysis with $\nu_0=36\,200$ or under the assumption that the final state of the λ 2785–2731 bands is X. The location of the state at $T_e=51\,847$ cm^{-1} is too high to permit its identification as 1432, $^3\Pi_{1g}$ or $^1\Pi_g$ in view of the evidence that T_e of $^3\Pi_0^+{}_g$ is 41 411 cm^{-1} (or, if Verma's analysis of the λ 3425 bands is correct, at 45 937 but, if so, mixed with 2242, $^1\Sigma_g^+$—see above) and also in view of the locations of the 1432, $^3\Pi_{2g}$ and $^3\Pi_{1g}$ states as indicated by the interpretation of the absorption spectrum (see Table IV below). The energy height $T_e=51\,847$ is, however, about right for the Rydberg state 243(6s), $^3\Pi_0^+{}_g$, but unfortunately the ω_e value of the state is too small and the shape of the Franck–Condon parabola is not right; and the reported bands do not appear to lend themselves to a re-analysis with the required characteristics for a transition from a Rydberg state to either state B or state X. Wieland (private communication) proposes that both the initial and final states are ion-pair states. Reference to Fig. 1 suggests that 0442, $^1\Sigma_g^+\rightarrow1441$, $^1\Sigma_u^+$ might be a possibility.

It is instructive to survey the energy values which can be deduced for various ion-pair states on the basis of the conclusions and proposals presented in Secs. VI–VIII. This is done in Table IV, where observed or estimated vertical energies T_v are compared with potential-minimum energies T_e for several ion-pair states. For these, as expected, the differences $T_v - T_e$ are rather large, in contrast to non-ion-pair states, for a few of which data are included in the table. In evaluating the varying values of $T_v - T_e$ for the ion-pair states, it must be kept in mind that the T_v values are only estimates, and some of the other values are not certain. Further, it should be recognized that the T_e values for ion-pair states are probably determined much more by the dissociation asymptotes toward which they tend than by their electron configurations at small R values.

The basis for Table IV is largely self-explanatory except that something must be said about how the T_e values for 1432, $^3\Pi_{2g}$ and $^3\Pi_{1g}$ were arrived at. For $^3\Pi_{2g}$, $\nu = 29\,200$, the equivalent of $\lambda\,3427$, the low-frequency edge of the $^3\Pi_{2g} \leftarrow {}^3\Pi_{2u}$ absorption region, is added to an estimated 1000 cm^{-1} for the distance of this edge from the 0, 0 band and to 10 100 cm^{-1} for the height of the minimum of $^3\Pi_{2u}$ above that of X, giving 40 300 cm^{-1}. For $^3\Pi_{1g}$, similarly, to 30 600, corresponding to $\lambda\,3263$, is added 500 and 11 200, giving 42 300 cm^{-1}. The results are estimates but should not be far wrong. In Table IV, the location of ν_e of 1432, $^3\Pi_0{}^+{}_g$ relative to 1432, $^3\Pi_{2g}$ and $^3\Pi_{1g}$ is anomalously low if the E level is identified with $^3\Pi_0{}^+{}_g$, and this anomaly is not explained by a difference in predicted dissociation products. The anomaly is removed if the location of ν_e of $^3\Pi_0{}^+{}_g$ corresponding to Verma's analysis of the $\lambda\,3425$ bands as $^3\Pi_0{}^+{}_g \rightarrow {}^3\Pi_0{}^+{}_u$ is accepted.

Surveying all the evidence so far presented, it does not seem possible to make a decision between Verma's analysis of the $\lambda\,3425$ bands and Tellinghuisen's proposal according to which they are 1432, $^3\Pi_{2g} \rightarrow 2431$, $^3\Pi_{2u}$. One is tempted to suppose that, by coincidence, bands of both of these transitions are present, as well as to a certain extent, depending on experimental conditions, also D→X bands (especially in Wieland's Spectrum II). The reader should look for further elucidation in forthcoming papers[59] by Wieland, Tellinghuisen, and Nobs; but further experimental investigation will also be necessary.

Further, the exact location of T_0 of the D level remains doubtful. Wieland's Eq. (12) has no certain basis with respect to the v' numbering. The considerations of Sec. VII which lead to a T_0 value near 42 000 are quantitatively somewhat uncertain. A lower value together with smaller R_e than the value of 4.1 Å arrived at in Sec. VII, would be much more compatible with a reasonable $U(R)$ curve leading toward the probable dissociation asymptote $^3P_0 + {}^1S$ (see Table I). Reasonable values might be $T_0 \approx 41\,000$ cm^{-1} and $R_e \approx 3.8$ Å. Figure 1 has been drawn accordingly. The low value of $T_v - T_e$ for state D in Table IV suggests that T_0 might

be lower still, but since the T_v values except for the D level are only estimates, this point should not be given great weight.

In connection with Table IV, some of Elliott's observations on the behavior of the bands discussed above under increasing nitrogen pressure should be considered. Approximately quoting Elliott, the $\lambda\,3425$ region "is very weak at low nitrogen pressures, and increases in intensity with increasing nitrogen pressures up to about 2 cm of mercury. At higher pressures, the intensity of the higher frequency part of this system is reduced, but the intensity of the maximum increases slowly up to at least 1 atm. of nitrogen." The decreasing intensity of the higher-frequency part of the $\lambda\,3427$ region can be understood if that part corresponds to higher v' values, and collisions reduce higher to lower v' values. Further, the $F \rightarrow X$ system "first appears distinctly about 10 cm pressure of nitrogen and does not alter greatly in intensity when the pressure is increased to 1 atm." The $E \rightarrow B$ system "suffers a considerable reduction in intensity when the nitrogen pressure is increased from 10 cm of mercury to 1 atm."

If the E level, for which T_e is definitely 41 411 cm^{-1}, is $^3\Pi_0{}^+{}_g$, and the upper level of the $\lambda\,3427$ band is $^3\Pi_{2g}$ with $T_e \approx 40\,300$, one might interpret the decreasing intensity of the $E \rightarrow B$ transition with increasing nitrogen pressure as due to collisional degradation from $^3\Pi_0{}^+{}_g$ to $^3\Pi_{2g}$. The absence of $^3\Pi_{1g} \rightarrow {}^3\Pi_{1u}$ bands could then be attributed to the higher energy of $^3\Pi_{1g}$ for which $T_e \approx 42\,300$. The absence of D→X bands if T_e of D is at 41 000 could not be very well explained, however, unless T_e of D is higher, but this possibility seems rather unlikely (see above). The fact that $^3\Pi_0{}^+{}_g$ is at 45 937 if Verma's analysis of the $\lambda\,3425$ bands is correct would not be explained, since now this level would be above the E level. On the other hand, the F level *certainly* is above the E level, yet its intensity is not decreased by collisional degradation at higher pressures of nitrogen. On the whole, although the idea of collisional degradation from higher to lower electronic states is appealing, the evidence does not appear to justify definite conclusions based on this idea.

The mechanism by which foreign gases cause the diffuse bands to fade out and the four discrete band systems above discussed to appear is a matter of interest. In the case of fluorescent excitation at least, the initial excitation is to a D state level of high vibrational energy. In Elliott's experiments, with excitation by Al lines $\lambda\,1854$ and $\lambda\,1862$, E' would be between 53 000 and 54 000 cm^{-1}. After collisions with N$_2$ molecules, low vibrational levels[82,83] of the ion-pair states are produced ($v' = 0$–11 for E, 0–10 for F, 0–36 for the upper level of the $\lambda\,3425$ bands according to Verma's analysis, or 0–19 according to Wieland and Tellinghuisen,[59] and 0–14 for the upper state of the $\lambda\,2785$–2731 bands).

Now according to the identifications of the electronic states as given above, each of these is just one of several

states of a particular electronic configuration, all of which should be bound ion-pair states with more or less similar potential curves. Emission from many of these states should give rise to diffuse bands, e.g., the 1432, $^3\Pi_{0^-g}$ state should emit strongly to the repulsive 2431, $^3\Pi_{0^-u}$ state and $^1\Pi_g$ to $^1\Pi_u$, etc. It seems likely that transitions from all the states of each of the configurations which are represented at high foreign-gas pressure by discrete bands, may be present—although possibly this supposition is incorrect because of selection rules even in collisions. If it *is* correct, the secondary diffuse bands may be attributed to these and perhaps other states, reached by collisions even just between iodine molecules in the absence of foreign gases. It is then puzzling that the diffuse bands largely fade out in the presence of foreign gases at considerable pressures. Presumably the same states which give rise to the diffuse bands are also present but with decreased v' values in the presence of foreign gases. With lower v' values the positions of the resulting diffuse bands would of course be shifted, and possibly their superposition leads to a structureless background continuum.

A final answer must await further study. In such a study, the iodine emission spectrum excited in active nitrogen, which differs considerably from that excited in fluorescence in the presence of nitrogen, or by electrical discharges in iodine or iodine plus argon, should be examined in detail.

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† For brief preliminary communication regarding Sec. VIII, see Chem. Phys. Letters 7, 11 (1970).

‡ Visiting Professor, Feb.–April, 1970.

[1] (a) R. S. Mulliken, Phys. Rev. 46, 549 (1934); (b) R. S. Mulliken, Phys. Rev. 57, 500 (1940).

[2] For the most accurate evaluation of the molecular constants and U(R) curve for state X, see R. J. LeRoy, J. Chem. Phys. 52, 2683 (1970).

[3] For the B state, see (a) J. I. Steinfeld, R. N. Zare, L. Jones, M. Lesk, and W. Klemperer, J. Chem. Phys. 42, 25 (1965); (b) J. I. Steinfeld, J. D. Campbell, and N. I. Weiss, J. Mol. Spectry. 29, 204 (1969); (c) R. J. LeRoy and R. B. Bernstein, Chem. Phys. Letters 5, 42 (1970); (d) J. Mol. Spectry. 36, 3 (1970); 37, 109 (1971).

[4] D. C. Frost, C. A. McDowell, and D. A. Vroom, J. Chem. Phys. 46, 4255 (1967). The energy difference $^2\Pi_{(3/2)u} - ^2\Pi_{(3/2g)}$ is 1.54 eV, $^2\Pi_{1/2u} - ^2\Pi_{1/2g}$ is 1.72 eV.

[5] A. Recknagel, Z. Physik 87, 396 (1934).

[6] (a) For any $\pi\pi$ configuration, Recknagel shows that the energy is $C-(a-b)$, C, $C+(a-b)$, $C+2c-(a+b)$, $C+2c$, and $C+2c+(a+b)$ for the $^1\Sigma^-$, $^3\Delta$, $^3\Sigma^+$, $^3\Sigma^-$, $^1\Delta$, and $^1\Sigma^+$ states, respectively, where a, b, c are various specific integrals. For O₂, the near coincidence of the first three states shows that $a \approx b$. The $^3\Sigma^-$ minus $^3\Delta$ energy difference should then be $2c-(a+b) \approx 2c-2a = 1.7$ eV. The $^1\Delta$ minus $^3\Sigma^-$ and the $^1\Sigma^+$ minus $^1\Delta$ differences should each be $(a+b)$. Now for the integrals a and b

we have experimental data[7] for the N₂ molecule: $a=1.3$ and $b=0.9$ eV; for O₂ the values should be similar but somewhat greater, giving $a+b$ about, say, 2.7 eV. Applying the factor 0.37 as above, we arrive at estimates of 1.0 eV for the energy differences $^1\Delta$ minus $^1\Sigma^-$ and $^1\Sigma^+$ minus $^1\Delta$ in the 2332 configuration of I₂. (b) Dr. I. Hanazaki has very kindly gone through the calculations for the $\pi^3\pi^3$ case and shown that the results are exactly the same as for the $\pi\pi$ case.

[7] For a $\pi^3\pi$ configuration as in the 2310 configuration of N₂, Recknagel shows that the energy is $C-a$, C, $C+a$, $C+a$, $C+2b$, $C-a+4c$ for the respective states $^3\Sigma^+$, $^3\Delta$, $^3\Sigma^-$, $^1\Sigma^-$, $^1\Delta$, and $^1\Sigma^+$. The observed energy difference between the $^3\Sigma^-$ and $^3\Sigma^+$ states is 2.6 eV, which is $2a$. The difference between $^1\Delta$ and $^3\Sigma^-$ yields $2b-a=0.5$ eV, from which $b=0.9$ eV.

[8] (a) J. K. Knipp, Phys. Rev. 53, 734 (1938); (b) T. Y. Chang, Rev. Mod. Phys. 39, 911 (1967).

[9] In case the 2332 states $^1\Sigma_u^-(0_u^-)$ and/or $^3\Sigma_u^+(0^-$ and $1_u)$ were lower in energy than 1441, $^3\Sigma_u^+$, as has sometimes been suggested, the correlations in Fig. 1 would have to be changed, but these possibilities are here deemed rather strongly improbable (cf. Sec. VI).

[10] The validity of this assumption is uncertain. It was based on the following thought: The repulsion energy of two He atoms (MO configuration $\sigma_g 1s^2\sigma_u 1s^2$) at 0.75 Å is about the same (about 10 eV) as the repulsion energy of two H atoms in the $\sigma_g 1s\sigma_u 1s$, $^3\Sigma_u^+$ state at 0.75 Å.

[11] For $\langle r^2 \rangle$ the value 7.2 a.u. calculated by C. F. Fisher [cf. Can. J. Phys. 46, 2336 (1968)] has been assumed. An older value of 6.2 a.u. is given by Knipp.[8a] In Table II, it is assumed that the states dissociate as indicated in Table I. However, in case the order of states of given case c character is actually reversed, the corresponding coefficients in Table I would be interchanged. For example, if 2341, $^3\Pi_{0^+g}$ lies below 2422, $^3\Sigma_g^-(0^+)$ instead of above it as estimated in Table I, the corresponding coefficients in Table II (together with their dissociation products) would be interchanged.

[12] See Refs. 41 and 46 in R. J. LeRoy and R. B. Bernstein, J. Chem. Phys. 52, 3869 (1970).

[13] R. J. LeRoy, J. Chem. Phys. 52, 2678 (1970).

[14] L. Brewer, R. A. Berg, and G. M. Rosenblatt, J. Chem. Phys. 38, 1381 (1963).

[15] A. Chutjian, J. K. Link, and L. Brewer, J. Chem. Phys. 46, 2666 (1967).

[16] A. Chutjian and T. C. James, J. Chem. Phys. 51, 1242 (1969).

[17] A. Chutjian, J. Chem. Phys. 51, 5414 (1969). See p. 5419 for estimate of intensity of continuum of $^1\Pi_u \leftarrow X$ absorption.

[18] J. I. Steinfeld and W. Klemperer, J. Chem. Phys. 42, 3475 (1965).

[19] J. I. Steinfeld, J. Chem. Phys. 44, 2740 (1966), and earlier references given there.

[20] J. E. Selwyn and J. I. Steinfeld, Chem. Phys. Letters 4, 217 (1969).

[21] J. I. Steinfeld, Accounts Chem. Res. 3, 313 (1970).

[22] E. Wasserman, W. E. Falconer, and W. A. Yager, J. Chem. Phys. 49, 1971 (1968); Ber. Bunsenges. Physik. Chem. 72, 248 (1968).

[23] G. E. Busch, R. T. Mahoney, R. I. Morse, and K. R. Wilson, J. Chem. Phys. 51, 837 (1969).

[24] E. O. Degenkolb, J. I. Steinfeld, E. Wasserman, and W. Klemperer, J. Chem. Phys. 51, 615 (1969). For earlier work, see references given there.

[25] W. M. Huo, J. Chem. Phys. 52, 3110 (1970).

[26] (a) See Ref. 16, p. 1247. Further, J. B. Tellinghuisen, Ph.D. thesis, University of California, Berkeley, November, 1969. (b) R. J. Oldman, R. K. Sander, and K. R. Wilson, J. Chem. Phys. 54, 4127 (1970).

[27] L. A. Turner, Z. Physik 65, 464 (1930) and references given there.

[28] J. H. Van Vleck, Phys. Rev. 40, 544 (1932).

[29] This they do not say explicitly, but they deduce a quantity g_{eff} whose observed value is compared with a value estimated theoretically in a previous paper[19] in which it was assumed that the predissociating state is 2332, $^3\Sigma_u^+(0^-)$.

[30] See reference to it on p. 555 of Ref. 28.

[31] As discussed above, most probably the 0_u^- curve which crosses the B curve is that from 1441, $^3\Sigma_u^+$, but *possibly* it is the 2332, $^1\Sigma_u^-$ or $^3\Sigma_u^+(0^-)$ curve.

[32] L. A. Turner, Phys. Rev. 41, 627 (1932).

[33] The 2341, $^3\Pi_{1g}$, for which $\Delta\Omega=1$, would also be very weakly possible. The selection rule $\Delta\Sigma=0$ (hence $\Delta\Omega=0$) holds for spectroscopic transitions between two case a $^3\Pi$ states; see G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, New York, 1950), 2nd ed., p. 242. The same rule should hold to some extent in case c; but in any event, the strongest known $\Omega\Delta=1$ transition in iodine, $^1\Pi_u\leftarrow X$ (see Sec. V) is weak.

[34] Steinfeld[21] shows the 2341, $^3\Pi_{0^+g}$ curve as running entirely *below* the B curve, which would be very unfavorable for collisional predissociation. But such a location of this $^3\Pi_{0^+g}$ curve seems to be clearly excluded by the considerations on which Table I and Fig. 1 are based.

[35] The estimated vertical energy of 2341, $^3\Pi_{0^+g}$ is only 0.3 eV above that of $^3\Sigma_g^-(0^+)$ in Table I, and a reversed order is almost as likely as not. If the order were reversed, the $^3\Pi_{0^+g}$ curve would dissociate to two $^2P_{3/2}$ atoms, crossing the B curve a little above where the $^3\Pi_{1g}$ crosses.

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

[37] L. Mathieson and A. L. G. Rees, J. Chem. Phys. **25**, 753 (1956). See Fig. 3(a) for the $^3\Pi_1\leftarrow X$ absorption.

[38] Thesis,[26a] p. 136. An exact value is difficult to determine because the weak continuum of $^3\Pi_1\leftarrow X$ overlaps the much stronger absorption of the B$\leftarrow X$ bands.

[39] Other interactions with higher-energy states should be included in a complete configuration–interaction calculation, but we may assume these to be about the same for $^3\Pi_1$ and $^1\Pi$.

[40] References 36 and 37 are in good agreement on the value 17.7×10^{-4} Å, as estimated from their absorption curves. However, Tellinghuisen estimates a somewhat higher value, perhaps 19×10^{-4} Å.

[41] The dipole strengths for $^3\Pi_1\leftarrow X$ and $^1\Pi\leftarrow X$ are given as $2D$ because of the twofold degeneracy of $^3\Pi_1$ and $^1\Pi$, where D refers to a single component. On the other hand, $^3\Pi_{0^+}$ is nondegenerate.

[42] R. S. Mulliken, J. Chem. Phys. **7**, 20 (1939).

[43] Van Vleck (Ref. 28, p. 554) argues against an important contribution of $^3\Pi_{0^+g}$ character in X to the intensity of B$\leftarrow X$, but a careful consideration of all that is involved (among other points, the presence of a selection rule[33] forbidding $^3\Pi_{1u}\leftrightarrow^3\Pi_{0^+g}$ in case a and thereby indicating weakness in case c) shows that his argument is invalid.

[44] The matrix element between ψ_1° and ψ_2° is zero; they are mixed only indirectly via ψ_3°.

[45] This value is based on Julien and Person's value[46] of 0.43 for the oscillator strength of 1441, $^1\Sigma_u^+\leftarrow X$, with $\nu=5.48\times10^4$ for this transition (see Sec. VI for discussion).

[46] L. M. Julien and W. B. Person, J. Phys. Chem. **72**, 3059 (1968).

[47] J. A. Myer and J. A. R. Samson, J. Chem. Phys. **52**, 716 (1970).

[48] P. Venkateswarlu, Proc. Indian Acad. Sci. **A24**, 473 (1946).

[49] P. Venkateswarlu, Indian J. Phys. **21**, 43 (1947).

[50] P. Venkateswarlu, Can. J. Phys. **48**, 1055 (1970).

[51] The vertical energies at R_e of state X should be somewhat less than those given by ν_{max} since the first peak of the vibrational wavefunction at the inner limb of the upper $U(R)$ curve, which approximately determines the position of ν_{max}, is somewhat outside the point of intersection of the vibrational energy level with the $U(R)$ curve. This difference has been ignored here in Table I in the case of the 1441, $^1\Sigma_u^+$ state. For the $^3\Sigma_u^+(1)$ curve, it is taken into account by utilizing the segment of $U(R)$ curve deduced by Mathieson and Rees.

[52] M. Tamres, W. K. Duerksen, and J. M. Goodenow, J. Phys. Chem. **72**, 966 (1968); A. A. Paschier and N. W. Gregory, *ibid.* **72**, 2697 (1968); and references given in these papers.

[53] A transition of this type (2310, $^1\Sigma_u^-\leftarrow2400$, $^1\Sigma_u^+$) is known in N_2 [P. G. Wilkinson and R. S. Mulliken, J. Chem. Phys. **31**, 674 (1959) and S. G. Tilford and P. G. Wilkinson, Astrophys. J. **141**, 427 (1965)], but is *excessively* weak, and due only to rotational perturbation.

[54] H. Sponer and W. W. Watson, Z. Physik **56**, 184 (1929); H. Cordes, *ibid.* **97**, 603 (1935). At shorter wavelengths are several systems some, at least, of which are Rydberg bands (for a pictorial representation, see Ref. 47).

[55] P. Pringsheim and B. Rosen, Z. Physik **50**, 1 (1928); "PR bands." M. Kimura and M. Miyanishi, Sci. Papers Inst. Phys. Chem. Research (Tokyo) **10**, 33 (1929); "KM bands."

[56] W. E. Curtis and S. F. Evans, Proc. Roy. Soc. (London) **A141**, 603 (1933).

[57] D. T. Warren, Phys. Rev. **47**, 1 (1935).

[58] A. Nobs and K. Wieland, Helv. Phys. Acta **39**, 564 (1966). See also Ref. 59.

[59] K. Wieland, report at Euchem Conference on Molecular Spectroscopy, Cirencester, England, 13–17 July 1970. His observations and conclusions about the ultraviolet absorption and emission spectrum of natural and isotopic iodine are to be published in three consecutive papers jointly with J. Tellinghuisen and A. Nobs.

[60] Other values are 0.2 according to B. J. Huebert and R. M. Martin, J. Phys. Chem. **72**, 3046 (1968), but their value was incidental to another investigation and seems to have been only very roughly determined; 2.3 according to N. S. Bayliss and J. V. Sullivan, J. Chem. Phys. **22**, 1615 (1954), but this value is unbelievably high. J. B. Tellinghuisen[26a] gets a much smaller value, but has used very rough assumptions.

[61] W. B. Person (private communication).

[62] The same effect has been observed by others, e.g., R. Millikan (private communication).

[63] In particular, note the discordant interval 187 cm^{-1} between the $\nu=53\,782$ and 53 969 bands in the $v''=1$ column where all the neighboring intervals are near 140 cm^{-1}, likewise the discordant interval 96 cm^{-1} between the 53 827 and 53 923 bands in the $v''=3$ column where all the neighboring intervals are near 140 cm^{-1}. These discrepancies are far too large to be accounted for by experimental error, whereas Eq. (11) represents all the bands but the first two (out of 94 Fk Cordes bands) with an average discrepancy of something like ±5 cm^{-1}.

[64] R. D. Verma, J. Chem. Phys. **32**, 738 (1960). References to earlier work are given there.

[65] K. Wieland and J. Waser, Phys. Rev. **85**, 385 (1952).

[66] Cf. A. G. Gaydon, *Dissociation Energies* (Chapman and Hall, London, 1968), 3rd ed., p. 105.

[67] E. Skorko, Nature **131**, 366 (1933); Acta Phys. Polon. **3**, 191 (1934).

[68] K. Wieland (private communication, 1970).

[69] Transitions $^3\Pi_{2g}\leftarrow^3\Pi_{1u}$ and $^3\Pi_{1g}\leftarrow^3\Pi_{2u}$ should be much weaker since there is a strict selection rule $\Delta\Sigma=0$ in case a, hence $\Delta\Omega=0$ if $\Delta\Lambda=0$ as here [cf. G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, New York, 1950), pp. 242–3], although $\Delta\Omega=\pm1$ becomes possible in case c as here, such transitions should be relatively weak, especially in view of the fact that the only known $\Delta\Omega=\pm1$ transitions in I_2 (in particular, 2431, $^1\Pi_u\leftarrow X$) are weak.

[70] J. C. McLennan, Proc. Roy. Soc. (London) **A88**, 289 (1913); **A91**, 23 (1914).

[71] O. Oldenberg, Z. Physik **18**, 1 (1923).

[72] F. Duschinsky, E. Hirschlaff, and P. Pringsheim, Physica **2**, 439 (1935).

[73] F. Duschinsky and P. Pringsheim, Physica **2**, 633 (1935).

[74] O. Oldenberg, Z. Physik **25**, 136 (1924).

[75] F. Duschinsky and P. Pringsheim, Physica **2**, 923 (1935).

[76] A. Elliott, Proc. Roy. Soc. (London) **A174**, 273 (1940).

[77] M. Kimura and K. Tonomura, *Pieter Zeeman Volume* (Nijhoff, The Hague, 1935), p. 241.

[78] K. Asagoe, Sci. Repts. Tokyo Bunrika Daigaku **2**, 9 (1935).

[79] K. Asagoe and Y. Inuzuka, Sci. Repts. Tokyo Bunrika Daigaku **2**, 73 (1935). See, W. Finkelnburg, Phys. Zeits. **31**, 1 (1935) for a review of earlier work.

[80] R. K. Asundi and P. Venkateswarlu, Nature **156**, 452 (1945); P. Venkateswarlu, Proc. Indian Acad. Sci. **A24**, 480 (1946); **A25**, 119, 133 (1947).

[81] J. Waser and K. Wieland, Nature **160**, 643 (1947).

[82] P. Venkateswarlu, Phys. Rev. **81**, 821 (1951).

[83] R. D. Verma, Proc. Indian Acad. Sci. **A48**, 197 (1958).

[84] R. J. Strutt and A. Fowler, Proc. Roy. Soc. (London) **A86**, 105 (1912).

[85] Preceded by a few weaker anti-Stokes lines beginning at 1860 Å.

[86] Oldenberg reported some overlapping of continuous background and diffuse bands beginning at λ 2042.

[87] McLennan reported diffuse bands extending from 2100 Å to 4600 Å. McLennan did not find the resonance series below λ 2100, but this is explained by the fact that he did not use Schumann (gelatin-free) plates, as Oldenberg[71] did.

[88] Bhatnagar *et al.* Phil. Mag. **5**, 1226 (1928).

[89] H. Kuhn, Z. Physik **63**, 458 (1930).

[90] R. S. Mulliken, J. Chem. Phys. **55**, 309 (1971), following paper.

[91] E' cannot be exactly determined from these data since for the longer exciting wavelengths, heated iodine was used, and excitation must have come from initially vibrating molecules. Here absorption must be in the KM and PR bands. In any event, E' is obviously smaller for the longer exciting wavelengths.

[92] Reference 90, Eqs. (23) and (25).

[93] The change in L^* in Eq. (13) is less important for $\delta\nu$ than the change in E' since L^* is not very sensitive to E''.

[94] Here the quantity $\delta=\frac{1}{2}k(R-R_e)^2$ is small, so that the harmonic approximation is accurate enough for present purposes.

[95] A. G. Briggs and R. G. W. Norrish, Proc. Roy. Soc. (London) A276, 51 (1963).

[96] R. S. Mulliken, Chem. Phys. Letters 7, 11 (1970) for a brief preliminary communication regarding this section.

[97] A. Elliott, Ref. 76. Elliott also found another system 4030–4440 Å, but this is not present in later work[57] on iodine in argon, and this system has been attributed to a molecule IN.

[98] J. B. Tellinghuisen (private communication, 1970); and see Tellinghuisen's thesis,[26a] p. 152.

[99] With respect to expected shortcutting into excited atoms, see the last paragraph of Sec. III.

[100] According to a calculation by N. S. Ham (see Ref. 37, footnote on p. 756), $I^+ \, {}^1S$ is 84% ^1S and 16% $^3D_0$, so that $^3P_0$ would be 84% $^3P_0$ and 16% ^1S; and for $^3P_2$ and ^1D there is a 9.5% mixing.

Role of Kinetic Energy in the Franck–Condon Principle*

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During an electronic transition in a molecule the nuclear positions and momenta (hence kinetic energies) both tend to remain fixed according to the Franck principle. According to the quantum mechanical Franck–Condon principle, the *most probable* changes in vibrational quantum numbers or nuclear energy conform to the Franck principle. As usually implemented, it is assumed that the most probable nuclear-energy transitions are approximately at frequencies corresponding to the R values (R=internuclear distance) of classical turning points of the nuclear motion, where the classical kinetic energy is zero. It is shown here for some model diatomic cases that, in transitions to or from a bound state with enough vibrational energy, an equally strong maximum of transition probability as a function of frequency can occur classically corresponding to R values where the nuclei in the initial state have maximum kinetic energy. Quantum mechanically, this means for example that in such cases, transitions to states of the final-state continuum with considerable kinetic energy can have a relatively high probability if the potential curves of the two electronic states differ strongly in a suitable way. Formulas for the "fluctuation intervals" between diffraction maxima in the intensity structure of the continuum are derived. Applications to the observed emission spectrum of the iodine molecule are made in an accompanying paper.

In the application of the Franck–Condon principle[1] relatively little attention has been paid to the role of kinetic energy. The Franck principle states that when an electronic transition occurs in a molecule, the positions and momenta (hence, the kinetic energies) of the nuclei tend strongly to remain constant. Hence, in the quantum mechanical Franck–Condon principle for an electronic transition, nuclear transitions which correspond to classical conservation of position and kinetic energy are the most probable. However, because of the uncertainty principle, other nuclear transitions also occur. In this paper we explore the nature of the correspondence, with emphasis on initial states of high vibrational energy, for a diatomic molecule. Applications to the observed emission spectrum of the iodine molecule are made in the preceding paper.[2]

Let us assume the validity of the Born–Oppenheimer approximation and leave aside nuclear rotation as of minor relevance. Then the probability per unit time of an emission transition between two levels with electronic wavefunctions ψ' and ψ'' and nuclear wavefunctions χ' and χ'' is

$$dp/dt = C\nu^3 [\int\int\psi'(q, R)\chi'(R)\mu_{op}\psi''(q, R)\chi''(R)\,dq\,dR]^2, \quad (1)$$

where q refers to the electronic coordinates, μ_{op} to the electronic dipole moment operator, and R is the internuclear distance.

Integrating over the electronic coordinates,

$$dp/dt = C\nu^3 [\int Q_{el}(R)\chi'(R)\chi''(R)\,dR]^2. \quad (2)$$

While remaining aware that in general Q_{el} may depend considerably on R, we assume it constant for the present discussion. Then

$$dp/dt = CQ_{el}^2\nu^3 [\int\chi'(R)\chi''(R)\,dR]^2. \quad (3)$$

The integral here is the Franck–Condon overlap integral.

Three cases will be considered, corresponding to Figs. 1–3. For simplicity the bound upper state is shown as having a potential function $U'(x)=\frac{1}{2}kx^2$, where $x=R-R_e$, but the main features of the discussion are applicable for more realistic forms of $U'(x)$. For the lower state in Figs. 1–3, respectively, $U''(x)$ is taken as independent of x, as that of a repulsion curve, and as that of a bound state. With suitable changes, the results of the discussion are applicable if the roles of $U'(x)$ and $U''(x)$ are interchanged.

We now consider transitions down from a single level of high vibrational quantum number v' and energy E'