

RESOLUTION OF AN ANCIENT SPECTROSCOPIC PUZZLE: THE D \rightarrow X SPECTRUM OF I₂

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The D \rightarrow X emission from low- v levels of the D state is discerned in the region $\lambda < 3280$ Å of the emission spectrum of I₂ in Ar. Analysis of 47 bands spanning $v' = 0-3$ yields the constants (in cm⁻¹), $T_e = 41027.3(5)$, $\omega_e = 95.0(3)$, and $\omega_e x_e \approx 0.16$.

1. Introduction

The D(0_u^+) state of I₂ has been known almost since the dawn of spectroscopy, from its involvement in the very strong D \leftarrow X($1\Sigma_g^+$) transition centered near 1830 Å [1]. For decades there was further speculation about the possible role of the D state in the emission spectrum of I₂ in inert buffer gas, with several authors interpreting the strong emission system near 3400 Å as D \rightarrow X (but with varying vibrational assignments) [1-4]. However, since the D \leftarrow X absorption accesses only high- v' levels ($\approx 100-260$) and the D \rightarrow X emission in buffer gas involves only low v' (see fig. 1), there was no clear connection between the absorption and emission spectra.

In a landmark paper in 1971, Mulliken [5] interpreted the long-known McLennan spectrum of I₂ below 3300 Å as the highly structured continuum of the D \rightarrow X transition from high- v' levels. (The discrete segment of this spectrum was already well known [6].) Mulliken's interpretation was supported through quantum spectral simulations [7], which also yielded a crude estimate of the location of the D-state minimum ($T_e \approx 41200$ cm⁻¹, $R_e \approx 3.56$ Å). Additional work led to a reassignment of the 3400 Å system as D'(2_g) \rightarrow A'(2_u) [8,9], and the suggestion that the D \rightarrow X transition was probably responsible for the weak peak near 3260 Å in the tails of the D' \rightarrow A' system [10]. Very high levels of the D state have also been reported in multiphoton ionization experiments [11], and very recently several low levels have been analyzed in fluorescence [12]. However, in *none* of these studies has the abso-

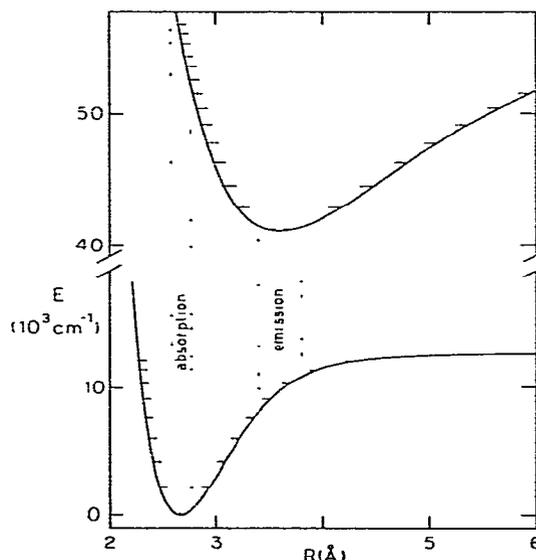


Fig. 1. Potential curves of D and X states of I₂, showing regions sampled in absorption and in high-pressure emission. The tick marks indicate every 10th v level in the X state, every 20th in D.

lute numbering of *any* D-state level been determined.

In the present paper I have scrutinized the 3100-3300 Å region of the emission spectrum of I₂ in Ar and have identified several progressions terminating on v'' levels 48-65 of the X state. From the intensity distributions and isotope shifts I can assign these transitions to v' levels 0-3. By a process of elimination the upper state can only be D(0_u^+), which becomes the last

state in the lowest cluster of six to be experimentally characterized near its minimum.

2. Results and discussion

Spectra were recorded as described previously [8–10], using a medium-resolution ($\approx 1 \text{ cm}^{-1}$) spectrometer to photograph the emission from Tesla discharge sources containing $^{127}\text{I}_2$ or $^{129}\text{I}_2$ in Ar ($>1/2 \text{ atm}$). The spectra were measured on a Grant comparator. In the spectral region of interest most of the features were less distinct than those at longer wavelengths; consequently the measurements carry a lower estimated precision of $1\text{--}2 \text{ cm}^{-1}$.

The ion-pair states of I_2 are spectroscopically "simple": They all have roughly the same ω_e ($\approx 100 \text{ cm}^{-1}$) and R_e ($\approx 3.6 \text{ \AA}$) values, and they cluster in accord with the energy of the I^+ atomic state with which they correlate [10, 13]. Guided by the anticipated similarity of the $\text{D} \rightarrow \text{X}$ spectrum to the well-known $\text{F} \rightarrow \text{X}$ system [14], I looked for progressions terminating on levels 45–65 of the X state. With the reduced precision of the measurements, and the spectral congestion in

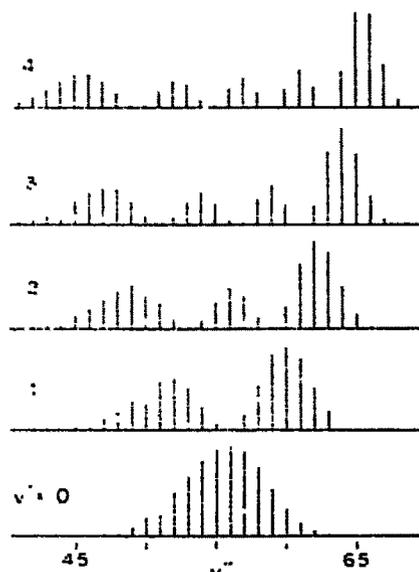


Fig. 2. Calculated Franck-Condon distributions for $\text{D} \rightarrow \text{X}$ emission from low- v' levels, assuming $R_e = 3.60 \text{ \AA}$. Note the characteristic reflection structure for this v' range.

this region, it was disturbingly easy to find *apparent* progressions containing four, five, and occasionally six members in this v'' range. Nevertheless the progressions identified for $v' = 0$ and 1 stood out as particularly convincing, with 12 consecutive members for the former, and nine for the latter displaying the expected Franck-Condon gap in the middle. For higher v' typically 4–7 members could be identified for each level up to $v' = 7$. Franck-Condon calculations (fig. 2) lent confidence to the assignments. However, for $v' > 3$ many of the predicted strong bands involving $v'' = 62\text{--}67$ coincided with already assignment bands in the $\text{D}' \rightarrow \text{A}'$ spectrum [8]. Without these bands I consider that levels $v' > 3$ cannot be assigned with certainty. For $^{129}\text{I}_2$ the spectra were not as good, and only levels 0–2 could be clearly identified. From the 47 assigned bands and the precisely known X-state energies [15], I have calculated the energies of the assigned v' levels. The results are given in table 1.

Because of the small range of D-state levels in table 1 and their low precision, least-squares fits showed little sensitivity to the constant $\omega_e x_e$. Thus I took the following approach: $\omega_e x_e$ was fixed at the value 0.16 cm^{-1} obtained from Rittner potential calculations for the D state, assuming $\omega_e = 95 \text{ cm}^{-1}$. (The Rittner potential yields reliable predictions of $\omega_e x_e$ for other known ion-pair states of I_2 [13].) With $\omega_e x_e$ thus fixed, a least-squares fit of all seven levels in table 1 (with inclusion of the isotopic ρ factor for $^{129}\text{I}_2$) gave $T_e = 41027.3 \pm 0.5 \text{ cm}^{-1}$ and $\omega_e = 95.0 \pm 0.3 \text{ cm}^{-1}$.

There is little question that the state I have found is the $\text{D}(0_u^+ \ ^3\text{P}_2)$ state [i.e. the 0_u^+ state which tends toward $\text{I}^- + \text{I}^+(\ ^3\text{P}_2)$]. The T_e and ω_e values make it distinct from the other five ion-pair states in this ener-

Table 1
Energies (cm^{-1}) and uncertainties (1σ) of observed levels of the $\text{D}(0_u^+)$ state of I_2 a)

v	$^{127}\text{I}_2$		$^{129}\text{I}_2$	
	no. of bands	E	no. of bands	E
0	12	41074.9(6)	6	41074.8(4)
1	9	169.5(4)	5	167.3(5)
2	7	264.2(7)	3	264.7(15)
3	5	358.0(7)		

a) Energies are relative to the minimum of the X state.

gy region, and they fall right where expected from Jaffe's theoretical predictions [16], calibrated against the other known states [17]. (A summary of the known ion-pair states and their spectroscopic constants is given in table 5 of ref. [17].) The energy for $v = 2$ is 2.3 cm^{-1} below that given for the lowest level observed by Koffend et al. [12], and the calculated energies for $v = 5$ and 6 are 0.1 and 3.0 cm^{-1} , respectively, below their other reported levels. Although the disparity is outside my 1σ errors in two of these three cases, the agreement is close enough to indicate that both studies have identified the same state. On the other hand my constants do not agree with those obtained by Chen et al. [18] from a study of three-photon intracavity absorption resonances ($T_e \approx 41049$, $\omega_e \approx 113$).

From Jaffe's predictions [16] and observations for other ion-pair states in the 41000 cm^{-1} region, I expect an internuclear distance very near 3.60 \AA for the D state. With spectra of this type one can usually fix R_e within 0.01 \AA by comparing calculated Franck-Condon distributions with observed. However, in the present case the progressions for $v' > 1$ are not sufficiently complete to permit such a precise determination, and I can only say that the observed intensity patterns are consistent with $R_e = 3.60 \pm 0.03 \text{ \AA}$. Similarly the long-wavelength cutoff of the spectrum at $\approx 3275 \text{ \AA}$ [which is associated with the minimum in the difference potential, $U'(R) - U''(R)$] is consistent with this value.

There remains the question of the correct numbering of the D-state levels observed in VUV absorption. According to a formula obtained by Wieland [19] and quoted by Mulliken [1], these levels are numbered ≈ 100 – 260 and range from 49115 cm^{-1} ($v = 100$) to 56950 cm^{-1} ($v = 260$) (energies relative to the minimum of the X state). My limited results do not provide a definitive answer to this question. However, by extending a plot of the high- v ΔG_v values to small v in such a way as to give the correct energy, ω_e , and $\omega_e x_e$ for the true $v = 0$, I conclude that Wieland's numbering is in fact very nearly correct (± 2 units). This result represents a fortuitous cancellation of errors, since Wieland designed his formula to represent a deeper state having a larger ω_e value [1]. I am continuing efforts to pin down the high- v numbering more precisely.

The observation of D \rightarrow X emission is in accord with the model developed in [10], whereby close-lying ion-pair states are assumed to be in thermal equilibrium in

the high-pressure limit. According to this model the D-state population is smaller than that of D' by a factor of ≈ 25 at 360 K , on the basis of Boltzmann factors and degeneracies. Its emission intensity is weaker still by a factor of 2 – 3 because of its smaller radiative decay rate [20–23]. It is nevertheless discernible in the spectrum, since it occurs so far in the wings of the D' \rightarrow A' spectrum. It should be mentioned that there is a *third* transition in this same region, namely $1_g(3P_2) \rightarrow A(1_u 3\Pi)$. With the renumbering and refined analysis of the $1_g(3P_2)$ state by Perrot et al. [24], most of the unassigned features in table 5 of ref. [9] can now be assigned to this transition with confidence. For this 1_g state the Boltzmann, degeneracy, and decay rate factors are more favorable, and $1_g \rightarrow A$ is predicted to have a total intensity $> 1/10$ that of D' \rightarrow A'. Indeed many of the observed $1_g \rightarrow A$ bands fall right in the region of strong D' \rightarrow A' emission.

3. Conclusion

The long-standing puzzle of the emission spectrum of I_2 in the 3000 – 3450 \AA region finally appears to be relenting to solution. The emission is dominated by D' \rightarrow A' at the long-wavelength end, with a weaker contribution from $1_g \rightarrow A$ in roughly the same spectral region and a much weaker contribution from D \rightarrow X further to the blue. I see no other transitions involving known states. This exclusion includes the recently discovered $0_g^+(3P_0) \rightarrow B(0_u^+)$ transition, which lies in this region but presumably is too weak from population and decay rate considerations [25–27]. However, it is worth noting that many line-like features in the 3200 – 3300 region remain unassigned, although they may be assignable to D' \rightarrow A' or $1_g \rightarrow A$.

With the determination of T_e and ω_e for the D state, it is now possible to much better define the D-state potential and refine the analysis of the D \rightarrow X and D \rightarrow a'(0_g^+) structured continua [7,28]. Work on these problems is in progress.

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References

- [1] R.S. Mulliken, *J. Chem. Phys.* 55 (1971) 288.
[2] A. Elliott, *Proc. Roy. Soc. A* 174 (1940) 273.
[3] P. Venkateswarlu, *Phys. Rev.* 81 (1951) 821.
[4] K. Wieland and J. Waser, *Phys. Rev.* 85 (1952) 385.
[5] R.S. Mulliken, *J. Chem. Phys.* 55 (1971) 309.
[6] R.D. Verma, *J. Chem. Phys.* 32 (1960) 738.
[7] J. Tellinghuisen, *Chem. Phys. Letters* 29 (1974) 359.
[8] J. Tellinghuisen, *Chem. Phys. Letters* 49 (1977) 485.
[9] J. Tellinghuisen, *J. Mol. Spectry.* 94 (1982) 231.
[10] A.L. Guy, K.S. Viswanathan, A. Sur and J. Tellinghuisen, *Chem. Phys. Letters* 73 (1980) 582.
[11] A.D. Williamson and R.N. Compton, *Chem. Phys. Letters* 62 (1979) 295.
[12] J. B. Koffend, A.M. Sibai and R. Bacis, *J. Phys. (Paris)* 43 (1982) 1639.
[13] J.C.D. Brand and A.R. Hoy, *J. Mol. Spectry.* 97 (1983) 379.
[14] K. Wieland, J. B. Tellinghuisen and A. Nobs, *J. Mol. Spectry.* 41 (1972) 69.
[15] J. Tellinghuisen, M.R. McKeever and A. Sur, *J. Mol. Spectry.* 82 (1980) 225.
[16] R.L. Jaffe, Paper MF5 at the 33rd Symposium on Molecular Spectroscopy (1978): private communication.
[17] K.S. Viswanathan and J. Tellinghuisen, *J. Mol. Spectry.*, to be published.
[18] K. Chen, L.E. Steenhoek and E.S. Yeung, *Chem. Phys. Letters* 59 (1978) 222.
[19] K. Wieland, unpublished.
[20] A.B. Callear, P. Erman and J. Kurepa, *Chem. Phys. Letters* 44 (1976) 599.
[21] M.C. Sauer Jr., W.A. Mulac, R. Cooper and F. Grieser, *J. Chem. Phys.* 64 (1976) 4587.
[22] J. Chevalyere, J.P. Perrot, J.M. Chastan, S. Valignat and M. Broyer, *Chem. Phys.* 67 (1982) 59.
[23] G.W. King, I.M. Littlewood and J.R. Robins, *Chem. Phys.* 68 (1982) 129.
[24] J.P. Perrot, M. Broyer, J. Chevalyere and B. Femelat, *J. Mol. Spectry.* 98 (1983) 161.
[25] H.P. Grieneisen and R.E. Francke, *Chem. Phys. Letters* 88 (1982) 585.
[26] J.C.D. Brand and A.R. Hoy, *Can. J. Phys.* 60 (1982) 1209.
[27] U. Heemann, H. Knockel and E. Tiemann, *Chem. Phys. Letters* 90 (1982) 17.
[28] K.P. Lawley, M.A. Macdonald, R.J. Donovan and A. Kvaran, *Chem. Phys. Letters* 92 (1982) 322.