

Observation and analysis of the $D' \leftarrow A'$ transition of I_2 in a free-jet expansion

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The A' state of I_2 is observed for the first time in a free-jet expansion, where it is prepared by ArF laser photolysis of I_2/Ar mixtures in the expansion region. Six bands in the $v''=0$ progression of the $D' \leftarrow A'$ transition are studied by laser excitation spectroscopy, leading to the following improved spectroscopic constants (cm^{-1}) for the A' and D' states: $B_0'' = 0.028054$, $B_0' = 0.020526$, $\alpha_0' = 5.30 \times 10^{-5}$, $\omega_e' = 103.953$, $\omega_e x_e' = 0.2097$, $\omega_e y_e' = 2.687 \times 10^{-4}$.

1. Introduction

Mulliken long ago predicted that the lowest excited electronic state in the diatomic halogens should be the $\Omega=2$ component of a $^3\Pi$ term ($2u\ ^3\Pi$ for the homonuclear species) [1]. However, radiative transitions between this state (now labeled A') and the ground $X\ ^1\Sigma^+$ state are strongly forbidden. Consequently A' remained unidentified prior to 1969, when it was assigned as the probable terminus of a strong UV emission spectrum from I_2 /inert gas discharges [2,3]. By the mid-70's this transition (now known as $D' \rightarrow A'$) and its counterparts in other halogens gained prominence as the operating media of new electronic transition lasers [4]. About the same time the A' state was also detected in infrared emission to X, from Cl_2 trapped in solid Ar [5]. Since that time the $D' \rightarrow A'$ transition has been analyzed vibrationally and/or rotationally in most of the diatomic halogens [6,7]; and $A' \rightarrow X$ emission has been detected for I_2 , Br_2 , IF , and IBr in rare gas matrices [8–12]. Meanwhile the prototype member of this family, $I_2(A')$, has come into prominence in other ways – as a possibly important player in the chemical

$O_2(^1\Delta)$ -pumped atomic iodine laser [13,14] and in the geminate recombination of I atoms in liquids [15–17].

In spite of the extended interest in the $D' \rightarrow A'$ transition, both of these states remain only sketchily characterized in most of the halogens [6]. The collisional processes that produce the $D' \rightarrow A'$ system in discharges also yield a vibrationally relaxed D' state. Thus emission from D' typically involves only a limited number of low v' levels; and because of the large decrease in internuclear distance from D' to A' , the emission accesses only an intermediate range of v'' levels. Special circumstances have permitted more extensive analyses of the A' states in I_2 [18] and ICl [19]. However, even in these cases the lowest vibrational level of A' remains unobserved. (In fact it is now known [20,21] that low levels of the A' states of Cl_2 and Br_2 were observed long ago in transient absorption from photoflashed halogen/rare gas mixtures [22]. However, at the time the absorption was attributed to the B state.)

In the present work we have achieved what we believe is the first observation of a halogen A' state in a supersonic free jet and have obtained thereby the first detailed spectroscopic characterization of $v=0$ in this state. For the halogen in question (I_2) we also

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obtain the first precise spectroscopic constants for the high- ν region of the ion-pair state D' ($2g^3P_2$) that is accessed in $D' \leftarrow A'$ absorption.

2. Experimental

Our experiment utilized the efficient though circuitous pumping process $X \rightarrow D(0^+u) \rightarrow D' \rightarrow A'$, that can be used to prepare $I_2(A')$ by ArF laser irradiation of I_2 in inert gases [20,21]. The free-jet expansion apparatus has been described previously [23]. I_2 vapor in equilibrium with the crystalline solid at room temperature was entrained in a flow of Ar carrier gas. The mixture was expanded through a 300 μm diameter nozzle into a chamber which was evacuated by a Roots blower. The expanding gases were excited by 193 nm light from an ArF laser (Lumonics TE860-4), using a 1 m focal length lens to focus the beam to a 1×10 mm rectangle ≈ 1 mm away from the nozzle, with its long axis perpendicular to the flow. The prompt fluorescence from this process was imaged onto the entrance slit of a 0.25 m monochromator (Jarrell-Ash 82-410, $f/3.5$) and detected by a photomultiplier (EMI 9558QB). A 295 nm long-pass filter in front of the monochromator discriminated against scattered 193 nm light. The signal from the photomultiplier was recorded by a boxcar integrator (SRS model 250) or a transient digitizer (LeCroy TR8837F, 32 MHz sampling rate). The spectra recorded in this manner bore a strong resemblance to those observed in discharges and in cell experiments and will not be discussed further here.

The same detection equipment was used to obtain the excitation spectrum of metastable species, which were excited with the frequency-doubled output from a tunable dye laser (Lambda Physik EMG101/FL3002E) focused into the expansion about 5–10 nozzle diameters downstream from the ArF laser beam. For proper synchronization this probe laser was fired 3–5 μs after the 193 nm laser. To detect the $D' \rightarrow A'$ fluorescence the monochromator was set near 340 nm, with a band pass of ≈ 4 nm; these conditions ensure that all excited ν' levels will be detected [18,21]. Survey spectra were taken over the 300–305 nm region at a probe laser bandwidth of 0.6 cm^{-1} . Selected bands identified in this region were then examined at 0.08 cm^{-1} resolution using an intracavity

etalon. The spectra were calibrated by simultaneously recording the $I_2 B \leftarrow X$ spectrum excited by directing the dye laser fundamental beam into an I_2 cell.

3. Results and discussion

Our survey spectra identified a number of red-degraded bands within 2–5 cm^{-1} of the expected positions for $D' \leftarrow A'$ $\nu' = 0$ bands, as predicted from vibrational constants that extend to $\nu' = 15$ [24,25]. (Note: the T_e'' value in footnote 21 of ref. [25] is erroneous; the correct value is 10041.2 cm^{-1} .) This leaves little doubt that we are observing the $D' \leftarrow A'$ system. Typical high-resolution results are illustrated by the 26–0 band displayed in fig. 1. For such spectra the calibration peaks were located by a simple three-point parabolic fit and were identified with the aid of the Gerstenkorn and Luc atlas [26]. Over the $\approx 10 \text{ cm}^{-1}$ ranges covered in these scans (in first order), typically 30–50 resolved calibration lines could be identified. The atlas wavenumbers for these were well fitted as linear functions of the channel number, yielding standard deviations of 0.003 – 0.005 cm^{-1} . With the correction of -0.0056 cm^{-1} [27], we take these figures as indicative of our absolute accuracy, too.

I_2 is a heavy molecule, and at our current resolution the $D' \leftarrow A'$ spectra remain afflicted by spectral congestion. For the low rotational temperatures of these spectra (≈ 5 K, see below), the P and R branches do not separate clearly for any of the six bands ($\nu' = 24, 26$ – 30) that we have recorded. Also, the Q branch, which is usually considered negligible for halogen $D' \rightarrow A'$ spectra, can contribute appreciably to the intensity near the band origin at these low T_s . Confronted with such congested spectra, we are unable to proceed via the usual “measure, assign, and fit” methods of conventional spectroscopic analysis. On the other hand, a typical spectrum does contain much high-quality information, in the form of ≈ 300 measurements of intensity as a function of a very precisely determined wavenumber. The problem is how to extract the information about energy levels (i.e. the spectroscopic constants) from such data.

To attack this problem we have employed nonlinear least-squares fitting methods similar to those

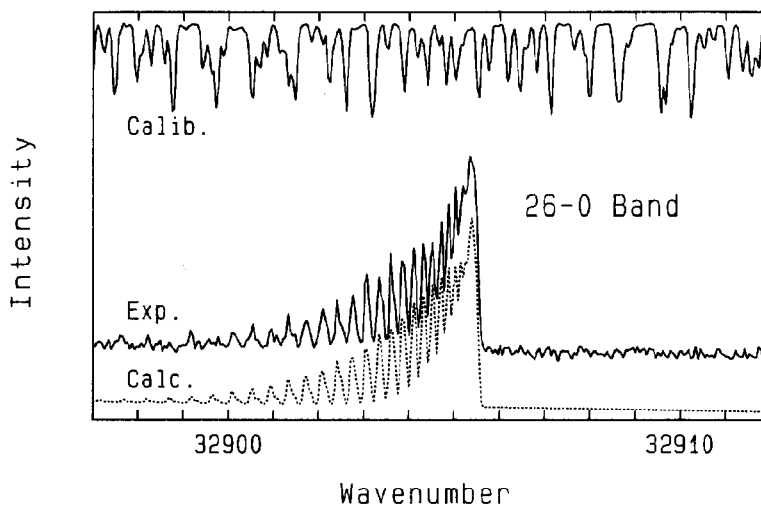


Fig. 1. Experimental and least-squares simulated spectra for the 26-0 band in the $D' \leftarrow A'$ spectrum of I_2 in a free-jet expansion. The spectroscopic parameters obtained from this fit are $\nu_0 = 32905.411(2) \text{ cm}^{-1}$, $B' = 0.019135(10) \text{ cm}^{-1}$, $T = 6.05(15) \text{ K}$, and $\text{fwhm} = 0.090(2)$. B'' was held fixed at 0.028054, and saturation was ignored. The first-order calibration spectrum is shown inverted at the top. The intensity scales are linear but otherwise arbitrary, except that the experimental $D' \leftarrow A'$ spectrum is displayed relative to a baseline value of zero.

which have been used recently to obtain population distributions from CN $B \rightarrow X$ spectra that are even more congested than these I_2 spectra [28]. However, in the CN case the spectral peak positions could be reliably computed from existing spectroscopic data, whereas in the present case we must extract positional and distributional information simultaneously. The advantage of such an analysis over conventional positions-only fitting is that we do obtain the population distributions as a bonus. Of course this is also a disadvantage, since an inadequate model for the intensities can confound the fitting, preventing convergence. The present fits included as many as 12 adjustable parameters: the band origin and rotational constants (B' and B''), four parameters to accommodate a $2-T$ rotational population distribution, a bandwidth, a saturation parameter, and three parameters to represent the background. Details about these fitting procedures will be presented elsewhere. However, the following points are worth noting:

(1) The saturation parameter allows for the transition from low-intensity excitation, where fluorescence is proportional to the product of absorption cross section and population, to high-intensity, where it is proportional to population alone. This affects

the Q branch directly, since the cross section does not depend strongly on J'' for the other branches. However, it also affects the apparent resolution for the P and R lines, because the half-width of the response function increases with saturation. The results of the fits suggest that the latter effect is more important for the current data, which means that the saturation parameter masquerades as a sort of second bandwidth. It also means that when saturation is important, the saturation and bandwidth parameters are strongly coupled, which makes convergence difficult to achieve. For this reason we dropped this parameter from the later fits, but we are continuing to examine its role in more controlled experiments.

(2) For the probe laser lineshape, we experimented with both triangular and Gaussian profiles. The latter is theoretically more sound and gave better convergence and more convincing results, so was used in the latter stages of the analysis. The bandwidth was retained as a free parameter, yielding $0.08\text{--}0.11 \text{ cm}^{-1}$ for the fwhm in most spectra, rising to 0.16 cm^{-1} for the 24-0 band, which seemed particularly poorly resolved. These values, which are generally precise to better than 10%, are somewhat larger than the manufacturer's nominal value (0.08 cm^{-1}). As noted above, the fitted bandwidth is a lumped pa-

parameter, containing contributions from saturation. Its excess over nominal and its band-to-band variation are consistent with the latter.

(3) The background is everywhere comparable in scale to the $I_2 D' \leftarrow A'$ spectrum (see fig. 1). All three parameters in its quadratic representation were statistically significant in most cases, although the curvature was only marginally so for several bands.

(4) Although we included provision for a 2- T rotational population distribution, we were able to obtain convergence for such distributions only by externally fixing both T s, in which cases we never obtained a significant reduction in the variance as compared with 1- T results. Hence we used just the latter in the final fits. The resulting values of T ranged 3.8–6.4 K; this is probably a manifestation of real changes in the experimental conditions, which were frequently readjusted to improve the signal.

(5) At our experimental resolution we must neglect effects such as Ω -doubling and hyperfine structure. The first consequence of both of these is a further broadening of the lines. The Ω -doubling is expected to be truly negligible for these $\Omega=2$ states at the low J values of our spectra, from what is known about this splitting in iodine [29] and in other halogens [6]. On the other hand, hyperfine structure in these charge-transfer transitions can span ≈ 0.05 cm^{-1} [30], so hyperfine broadening is likely contributing to our phenomenological bandwidths.

(6) For the low J values involved in our spectra, centrifugal distortion is almost negligible. Thus D'_v and D''_v were fixed at their calculated values, leaving only the band origin and rotational constants to locate the spectral peaks.

For strongly degraded bands the B' and B'' values are highly correlated, as their difference dominates in determining the line positions. Not surprisingly, there was considerable scatter in the band-by-band estimates of B'_0 in the present case. A weighted average of results for a Gaussian line shape with no saturation gave $B'_0 = 0.028054(16)$. Other assumptions about the line shape, band width, saturation, etc. yielded values larger by as much as $1.4 \times 10^{-4} \text{ cm}^{-1}$, so we consider this 1σ error estimate to be optimistic. Even so, the present value is already larger than the (extrapolated) value in ref. [18] by about 5 of their standard deviations. A similar discrepancy was noted for higher v'' levels in a recent rotational anal-

ysis of several $D' \rightarrow A'$ emission bands [31].

In a final fit for all six bands, we fixed B'' at the value given above to break the B'/B'' correlation. The B' values from these fits are plotted together with other results in fig. 2. A least-squares fit of our six values and the values of Lipson et al. [31] to a linear B_v relation yields $B_e = 0.020526(22)$, $\alpha_e = 5.30(9) \times 10^{-5} \text{ cm}^{-1}$. For obvious reasons the B_e value is virtually identical to that from ref. [31]; however, the α_e value is about 10% larger and substantially more precise. Given the imprecision in the existing estimates of B' for levels intermediate between $v' = 1$ and 24, there is no indicated need for terms beyond linear in the B'_v expression.

For reasons given elsewhere [25] the extensive band head data for $D' \rightarrow A'$, together with the absolute energies from the reassignment of the α state of King et al. [32] to D' , should better define the D' state T_v values than the more precise but sparsely sampled data from ref. [18]. By retaining the T_e and ω_e values from refs. [24,25] ($40388.24(10)$ and $103.953(26) \text{ cm}^{-1}$, respectively), we were able to represent the six new band origins with a maximum deviation of 0.013 cm^{-1} , in terms of a slightly al-

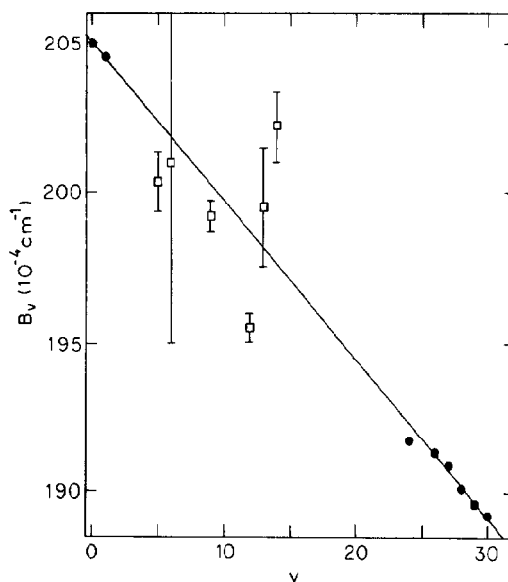


Fig. 2. Experimental estimates of B_v for D' -state v levels 0, 1, 5, 6, 9, 12–14, 24, and 26–30. The solid points, the first two of which are from ref. [31], were fitted to the indicated line; their individual errors are comparable to their displacement from this line. The values plotted with error bars (1σ) are from ref. [18].

tered ω_{ex_e} value and one additional parameter: $\omega_{ex_e}=0.2097(1)$, $\omega_{ey_e}=2.687(38)\times 10^{-4}$, where the quoted 1σ errors represent just the current fit results. These revised vibrational parameters affect G'_v negligibly in the $v'=0-15$ range of the vibrational analysis [24], and they reproduce the recent estimate [31] of the first vibrational interval almost exactly.

4. Conclusion

We have recorded and analyzed what we believe are the first high-resolution absorption spectra for the lowest excited electronic state in the diatomic halogens – the $A'(2(u)^3\Pi)$ state. The spectra are obtained for “cold” $I_2(A')$, prepared in the expansion region of a free-jet expansion via a novel fluorescence pumping technique. Analysis of the (still-congested) spectra by least-squares spectral simulation yields the first high-precision spectroscopic constants for the $v''=0$ and $v'=24-30$ regions probed in the experiments.

Near each $D'\leftarrow A'$ band in our survey spectra we have observed a companion band, whose position agrees within $\approx 1\text{ cm}^{-1}$ with predictions for the $v''=0$ progression of the $\beta(\lg^3P_2)\leftarrow A(1u^3\Pi)$ system [6]. The comparable intensities in these two systems is noteworthy, as it implies comparable populations in A and A' . Since the pumping scheme we have utilized should discriminate much more strongly in favor of A' , this may mean that these metastable states are being formed via atom recombination (following $D\rightarrow X$ fluorescence or prompt thermal dissociation of A'), or possibly that they undergo interconversion via collisions in the early stages of their relaxation. (Note that we observe no absorption from $v''>0$ in either system.) In that case we may expect to observe absorption from other weakly bound states near the first dissociation limit. We are currently searching for these as we attempt to expand our analyses of the $D'\leftarrow A'$ and $\beta\leftarrow A$ systems. We are also further investigating a broad emission peak near 400 nm, which is likely due to a moderate-sized cluster of I_2 in Ar undergoing the analogue of the $D'\rightarrow A'$ transition – and which interestingly is shifted from the 342 nm position for pure I_2 by even more than is the Ar-matrix isolation spectrum [11]. It is pos-

sible that this system is contributing to the strong background in our $D'\leftarrow A'$ excitation spectra.

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References

- [1] R.S. Mulliken, *Phys. Rev.* 57 (1940) 500.
- [2] J.B. Tellinghuisen, Ph.D. Thesis, University of California, Berkeley, CA, UCRL-19112, November, 1969.
- [3] R.S. Mulliken, *J. Chem. Phys.* 55 (1971) 288.
- [4] J. Tellinghuisen, *Pure Appl. Phys.* 43 (1982) 251.
- [5] V.E. Bondybey and C. Fletcher, *J. Chem. Phys.* 64 (1976) 3615.
- [6] J.C.D. Brand and A.R. Hoy, *Appl. Spectros. Rev.* 23 (1987) 285.
- [7] R.I. Narayani and J. Tellinghuisen, *J. Mol. Spectry.* 141 (1990) 79.
- [8] P. Beeken, M. Mandich and G. Flynn, *J. Chem. Phys.* 76 (1982) 5995.
- [9] P. Beeken, E.A. Hanson and G. Flynn, *J. Chem. Phys.* 78 (1983) 5892.
- [10] J.-P. Nicolai and M.C. Heaven, *J. Chem. Phys.* 87 (1987) 3304.
- [11] M. Macler and M.C. Heaven, *Chem. Phys.*, submitted for publication.
- [12] M.C. Heaven, to be published.
- [13] R.F. Heidner III, C.E. Gardner, G.I. Segal and T.M. El-Sayed, *J. Phys. Chem.* 87 (1983) 2348.
- [14] M. Nota, A.J. Bouvier, R. Bacis, A. Bouvier, P. Crozet, S. Churassy and J.B. Koffend, *J. Chem. Phys.* 91 (1989) 1938.
- [15] N.A. Abul-Haj and D.F. Kelly, *J. Phys. Chem.* 91 (1987) 5903.
- [16] A.L. Harris, J.K. Brown and C.B. Harris, *Ann. Rev. Phys. Chem.* 39 (1988) 341.
- [17] R. Lingle Jr., X. Xu, S.-C. Yu, H. Zhu and J.B. Hopkins, *J. Chem. Phys.*, in press.
- [18] J.B. Koffend, A.M. Sibai and R. Bacis, *J. Phys. (Paris)* 43 (1982) 1639.
- [19] J.C.D. Brand, D. Bussieres and A.R. Hoy, *J. Mol. Spectry.* 113 (1985) 388.
- [20] J. Tellinghuisen, A.R. Whyte and L.F. Phillips, *J. Phys. Chem.* 88 (1984) 6084.
- [21] J. Tellinghuisen and L.F. Phillips, *J. Phys. Chem.* 90 (1986) 5108.

- [22] A.G. Briggs and R.G.W. Norrish, *Proc. Roy. Soc. A* 276 (1963) 51.
- [23] L.J. van de Burgt and M.C. Heaven, *J. Chem. Phys.* 89 (1988) 2768.
- [24] J. Tellinghuisen, *J. Mol. Spectry.* 94 (1982) 231.
- [25] J. Tellinghuisen, *J. Chem. Phys.* 78 (1983) 2374.
- [26] S. Gerstenkorn and P. Luc, *Atlas du spectre d'absorption de la molécule d'iode (14800–20000 cm⁻¹)* (CNRS, Paris, 1978).
- [27] S. Gerstenkorn and P. Luc, *Rev. Phys. Appl.* 14 (1979) 791.
- [28] J. Xu, M.H. Mendenhall and J. Tellinghuisen, *J. Chem. Phys.* 93 (1990) 5281.
- [29] J.P. Perrot, B. Femelat, M. Broyer and J. Chevalerey, *Mol. Phys.* 61 (1987) 97.
- [30] H. Knöckel, H. Richter, M. Siese and E. Tiemann, *Mol. Phys.* 68 (1989) 917.
- [31] R.H. Lipson, A.R. Hoy and N. MacDonald, *Chem. Phys. Letters* 168 (1990) 25.
- [32] G.W. King, I.M. Littlewood and J.R. Robins, *Chem. Phys.* 56 (1981) 145.