Coincidence ion pair production (cipp) spectroscopy of diiodine†

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Coincidence ion pair production (I⁺ + I⁻) (cipp) spectra of I₂ were recorded in a double imaging coincidence experiment in the one-photon excitation region of 71 600–74 000 cm⁻¹. The I⁺ + I⁻ coincidence signal shows vibrational band head structure corresponding to iodine molecule Rydberg states (I⁺) crossing over to ion-pair (I⁺I⁻) potential curves above the dissociation limit. The band origin (ν₀), vibrational wavenumber (ν₀) and anharmonicity constants (ω₀, ξ₀) were determined for the identified Rydberg states. The analysis revealed a number of previously unidentified states and a reassignment of others following a discrepancy in previous assignments. Since the ion pair production threshold is well established, the electric field-dependent spectral intensities were used to derive the cutoff energy in the transitions to the rotational levels of the 7p(1/2) (ν' = 3) state.

I. Introduction

A large number of Rydberg states have been identified for the iodine molecule (I₂) by standard absorption spectroscopy and by REMPI. Interactions between Rydberg and ion-pair states are well known for the halogens as well as for the interhalogens. These have been found to occur either above or below the dissociation energy thresholds for ion-pair states. In the former case, ion pairs (AB → A⁺ + B⁻) are formed by bound Rydberg-to-free ion-pair state transitions, whereas in the latter case bound-to-bound (Rydborg to ion-pair state) state transfer occurs. Exciting I₂ into a bound high energy Rydberg state which interacts with an ion-pair state should simultaneously form positive and negative ions, I⁺ and I⁻ at discreet energies once the excitation energy goes above the respective ion-pair dissociation energy threshold. Kvaran et al. demonstrated this by vibrationally resolved excitation of I₂, where both I⁺ and I⁻ were formed above the dissociation threshold of about 72 150 cm⁻¹. They observed virtually identical ion yield spectra for both atomic ions (I⁺ and I⁻) in the excitation region above the ion pair threshold. Spectral analysis revealed series of overlapping Rydberg states converging to the molecular ion ground state.

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II. Experimental

The experiments were carried out with the DELICIOUS III double-imaging photoelectron photoion coincidence (i²PEPICO)
spectrometer on the DESIRS undulator beamline\textsuperscript{17} of Synchrotron Soleil, in France. The instrument has been described in detail elsewhere\textsuperscript{18} and only a brief summary of the relevant parts is given here. Briefly, crystals of iodine were sublimated in an oven kept at 80 °C in a stream of helium bath gas. The iodine gas entered the ionization chamber through a supersonic expansion of an I\textsubscript{2}/He mixture, through a 200 μm heated nozzle, kept at 90 °C. The supersonic beam was collimated with a double skimmer setup of the SAPHIRS molecular beam endstation.\textsuperscript{19} Typical pressures were $1.5 \times 10^{-3}$ mbar in the expansion, $3.5 \times 10^{-6}$ mbar in the differential pumping, and less than $9 \times 10^{-8}$ mbar in the ionization regions. Photons from the variable polarization undulator OPHELIE\textsuperscript{2} were dispersed by a 6.65 m normal-incidence monochromator with a 2400 lines per mm grating and focused onto a 200/300 μm (H/V) spot in the ionization region. The entrance and exit slits of the monochromator were set to 100 μm and 300 μm, respectively, providing an energy resolution of 9.7 cm\textsuperscript{-1} (1.2 meV) at 130 000 cm\textsuperscript{-1} (16 eV). To block out high-order harmonics, a gas filter located upstream of the beamline was filled with neon. For absolute energy calibration, the same gas filter was filled with krypton and its well-known absorption lines, corresponding to dips in the cation signal, because of the diminished photon intensity due to absorption by krypton in the gas filter, were used for calibration. Specifically, the $4p^5(2P^\text{1}/2)5s^0$–$4p^6(1S)$ (85 846.71 cm\textsuperscript{-1}) absorption lines were used for calibration as reported by Yoshino and Tanaka and later deposited into the NIST Atomic Spectra Database.\textsuperscript{20,21} To validate the accuracy of this calibration, the cipp spectral lines were cross-referenced against the Venkateswarlu spectra,\textsuperscript{1 vide infra.}

The DELICIOUS III spectrometer is composed of an electron velocity map imaging setup and a modified Wiley–McLaren time-of-flight 3D momentum imaging ion mass analyzer in a multistart–multistop coincidence detection mode. This setup produces a multi-dimensional coincidence data set, two cross sections of which yield photoion mass-selected photoelectron spectra, as well as mass spectra of internal energy-selected photoions. In the recently pioneered coincidence ion pair production (cipp) experiments, the same physical setup was utilized, except that anions were detected on the imaging electron detector, in coincidence with cations from the same ion pair production events, as explained in more detail in the first cipp publication.\textsuperscript{16} Ion pair production coincidences were registered at the calculated and experimentally confirmed time delay between the I\textsuperscript{−} and I\textsuperscript{+} ions, using raytracing simulations of the DELICIOUS III coincidence setup.

III. Results and analysis

The coincidence ion pair production experiments were carried out in an electric field and, as previously noted,\textsuperscript{16} the cipp spectral lines may be susceptible to Stark shifts. Therefore, the experiments were carried out at three different extraction fields: 17.7, 44.3, and 88.7 V cm\textsuperscript{-1}. Due to limitations on the available synchrotron beamtime, the whole spectral range (8.92–9.17 eV) was only covered in the 44.3 V cm\textsuperscript{-1} measurements. The 17.7 V cm\textsuperscript{-1} measurements were carried out in the 8.92–9.06 eV range. In order to assess the effect of higher electric field near the ion pair production threshold, we have also collected data with 88.7 V cm\textsuperscript{-1} field for the first 40 meV of the spectra. Fig. 1 shows the collected cipp spectra at the three extraction fields and a cursory comparison shows that, unlike...
the F$_2$ cipp spectra, the peaks do not shift significantly with the extraction field strengths. However, close to the ion pair production threshold, the peak intensities and peak shapes do exhibit field-dependence. The inset in Fig. 1 shows that the first major peak between 72 020–72 030 cm$^{-1}$ is diminished at low field, while the next peak and its shoulder between 72 045–72 065 cm$^{-1}$ is somewhat enhanced, when the spectra are normalized for matching peak intensities above 72 100 cm$^{-1}$.

**Spectral analysis**

The mid-field (44.3 V cm$^{-1}$) spectrum was used for spectral analysis. It is shown in Fig. 1 and 2 for the excitation region of 71 600–74 000 cm$^{-1}$. These show vibrational spectral bands due to transitions from the ground state I$_2$, X$^1\Sigma^+$($v^0 = 0$) to Rydberg vibrational states (I$_2^+$($v'$)) followed by a transfer to an ion-pair state (I-I') above its dissociation limit to form I$^+$ and I, i.e.,

1) $I_2 + h\nu \rightarrow I_2^{++}(v')$; photoexcitation

2) $I_2^+ \rightarrow I^+ I'$; state transfer

3) $I' I^+ \rightarrow I' + I$; dissociation

The band origin ($v^0_0$) of a Rydberg vibrational state (I$_2^+$($v'$)) can, to a first approximation, be expressed as,

$$v^0_0([\Omega_c]nl) = IE([\Omega_c]) - \frac{R_N}{(n - \delta_1)^2}$$

where $[\Omega_c]nl$ refers to a Rydberg state which converges to either of the two spin–orbit components $\Omega_c = \frac{3}{2}, \frac{1}{2}$ of the ground ionic state I$_2^+$($X^1\Pi_g$) in vibrational level $v^0 = 0$, for a Rydberg electron with principal quantum number $n$, in a molecular orbital $\lambda$, corresponding to an atomic orbital $l$. $IE([\Omega_c])$ is the ionization energy of I$_2$($X^1\Sigma^+_g$($v^0 = 0, j^0 = 0$)) to form I$_2^+$($[\Omega_c]$) for $v^0 = 0$, $R_N$ is the Rydberg constant (109 735.85 cm$^{-1}$) and $\delta_1$ is an $l$-dependent quantum defect value, which is a measure of how much a Rydberg series diverges from the corresponding hydrogen atom Rydberg series. The I$_2$ molecule is best described by Hunds case (c) in which case the total spin is not a good quantum number and singlet and triplet states are not distinguishable. Accepted values for the

![Fig. 2](image-url)

**Fig. 2** Coincidence ion pair production spectra of I$_2$ for the one-photon excitation region of 71 700–74 000 cm$^{-1}$ with assignments. (a) Vibrational band head assignments for the p series Rydberg states converging to the 3/2 spin–orbit ground state ion core. Lowest-energy vibrational quantum numbers ($v_{\text{min}}$), when larger than zero ($v'$) are marked. (b) Vibrational band head assignments for the f series Rydberg states converging to the 3/2 spin–orbit ground state ion core and assignment of the 5f orbital conforming to the 1/2 spin–orbit ground state ion core.
ionization energies of I₂ to form I₂⁺ \( \left( \Omega = \frac{3}{2} \right) \) of 9.3074 ± 0.0002 eV (75 069 cm⁻¹) and to form I₂⁺ \( \left( \Omega = \frac{1}{2} \right) \) of 9.950 ± 0.002 eV (80 252 cm⁻¹)²²,²⁴ were used. These differ significantly from the 9.3995 eV (75 814 cm⁻¹) and 10.0297 eV (80 895 cm⁻¹) values, respectively, used by Venkateswarlu,¹ which explains why the overall Rydberg state assignments needed to be revised. Δ₁ values of about 3.5 ± 0.1 and 0.93 ± 0.12 were reported by Venkateswarlu for \( p(l = 1) \) and \( f(l = 3) \) Rydberg

Table 1 Calculated and observed band origins (ν₀) based on quantum defect analysis (see eqn (1)) for spectral bands/peaks from the work of Venkateswarlu and ours (*). (a) np Rydberg series converging to the \( \Omega = 3/2 \) and 1/2 ionic states, (b) nf Rydberg series converging to the \( \Omega = 3/2 \) and 1/2 states of I₂⁺

(a)

| n | np (3/2); Δ₁ = 3.3313 | np (3/2); Δ₁ = 3.4687 | np (3/2); Δ₁ = 3.5394 | np (3/2); Δ₁ = 3.56812 |
|---|------------------------|------------------------|------------------------|------------------------|
| 6 | 59 660                  | 59 662                 | 57 942                 | 57 958                 |
| 8 | 59 660                  | 59 662                 | 57 942                 | 57 958                 |
| 10 | 72 601                 | 72 602*                | 72 497                 | 72 496*                |
| 12 | 73 203                 | 73 203*                | 73 135                 | 73 136*                |
| 14 | 73 608                 | 73 608*                | 73 562                 | 73 563*                |
| 16 | 73 895                 | 73 893                | 73 861                 | 73 863                |
| 18 | 74 105                 | 74 106                | 74 080                 | 74 081                |
| 20 | 74 263                 | 74 244                | 74 234                 | 74 234                |
| 22 | 74 385                 | 74 370                | 74 367                 | 74 367                |

(b)

| n | nf (3/2); Δ₁ = 0.84243 | nf (3/2); Δ₁ = 0.8636 | nf (3/2); Δ₁ = 0.8846 | nf (3/2); Δ₁ = 0.9672 |
|---|------------------------|------------------------|------------------------|------------------------|
| 4 | 64 063                  | 64 074                 | 63 914                 | 63 930                 |
| 6 | 64 063                  | 64 074                 | 63 914                 | 63 930                 |
| 10 | 72 175                 | 72 175*                | 72 135                 | 72 135*                |
| 14 | 73 612                 | 73 612*                | 73 403                 | 73 403*                |
| 18 | 74 005                 | 74 010                | 73 999                 | 73 999                |
| 22 | 74 188                 | 74 184                | 74 181                 | 74 181                |
| 26 | 74 327                 | 74 328                | 74 324                 | 74 324                |
| 30 | 74 435                 | 74 435                | 74 431                 | 74 431                |
| 34 | 74 521                 | 74 521                | 74 518                 | 74 518                |
| 38 | 74 649                 | 74 646                | 74 647                 | 74 647                |
| 42 | 74 697                 | 74 696                | 74 695                 | 74 695                |
| 46 | 74 736                 | 74 735                | 74 735                 | 74 735                |
| 50 | 74 777                 | 74 776                | 74 776                 | 74 776                |
| 54 | 74 799                 | 74 799                | 74 798                 | 74 798                |
| 58 | 74 824                 | 74 823                | 74 823                 | 74 823                |

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series of I₂, and judging from atomic energy levels, \( \delta_0 \) values of about 4.01, 3.57, 2.50 and 0.04 are expected for \( s(l = 0), p(1), d(2) \) and \( f(3) \) Rydberg electron iodine atom orbitals, respectively.

Determination of the band origins \( (\nu_0^l) \) was based on a search of band/peak series observed in our spectra as well as the absorption spectra for consistent and realistic values of \( \delta_0 \) (i.e., a quantum defect analysis). The experimental band/peak maxima were assumed to correspond to the band origin. This could be justified for our observed spectral bands by analysis of band shapes (see Fig. S1 and S2 in the ESI†). A total of 20 Rydberg state series were identified (see Table 1 and Fig. 2).

Eight Rydberg series were found to correspond to transitions to Rydberg orbitals \( (\delta_0 \) in the range of 3.33–3.57), for which four converge to the \( \Omega_e = 3/2 \) spin–orbit molecular ion state and four converge to the \( \Omega_e = 1/2 \) spin–orbit excited state. Further 12 Rydberg series were found to correspond to transitions to Rydberg orbitals \( (\delta_0 \) in the range of 0.84–1.03), with six series converging to each of the two spin–orbit ion states.

The \( (\nu, \pi, \sigma, \delta) \) configurations of the Rydberg states were further specified by energetic considerations based on,

(i) that the energy progression of Rydberg molecular states is analogous to that of the corresponding Rydberg atomic states, for \( s < p < d < f \).

(ii) that the energies change as \( \pi < \delta < \sigma \) for the \( f \) Rydberg series and as \( \pi < \sigma \) for the \( p \) series.23

Thus, series of \( f(\sigma, \pi, \delta) \) and \( p(\sigma, \pi) \) states were identified as listed in Table 1. Two series for each set of quantum numbers were identified due to the two possible spin states of the excited electron. Energy differences corresponding to the spin–orbit coupling for the \( p \) and \( f \) Rydberg electrons were found to be about 330 cm\(^{-1}\) and 1000 cm\(^{-1}\), respectively, virtually independent of \( \lambda(\sigma, \pi, \delta) \) for the same \( l \) (\( f \) or \( p \)). Judging from our observations the trends in (i)–(ii) are independent of the molecular ion core spin–orbit configuration \( ([1/2], [3/2]) \).

In combination with the quantum defect analysis of the band origins for \( \nu = 0(\nu_0^l) \), search for vibrational bands due to transitions to higher Rydberg vibrational states \( (\nu, \nu') > 0 \) was made (Fig. 3). This was guided by the assumption that the vibrational frequencies/wavenumbers are comparable to that of the ground neutral \( (\omega_a = 214.50 \text{ cm}^{-1} \text{ \( \dagger \)) and ionic \( (\omega_a^+ = 220–240 \text{ cm}^{-1} \text{ \( \dagger \))) molecular states. Finally, the observed spectrum was simulated by using the PGOPHER program.26 The simulation was performed by optimizing a fit of calculated and experimental spectra for the total spectral range. The calculated spectra were based on Franck–Condon factors for the absorption transition, using known vibrational constants for the ground state of I₂ and vibrational constants for the excited states as fit parameters. Voigt (a combination of Gaussian width contribution of 8 cm\(^{-1}\) and Lorentzian width contribution of 2 cm\(^{-1}\)) line profiles were used to represent the vibrational bands profiles (see Fig. 3 and 4). The fit analysis resulted in vibrational temperature \( (T_{\text{vb}}) \) of about 40 K. In some cases, significant difference in peak intensities was observed between the experimental and calculated spectra. This is not a surprise, since the cipp detection depends on the crossover from the Rydberg states to ion-pair states, in addition to absorption, whereas the simulation is based on the absorption cross-sections only. In particular we were unable to fit/explain an unusually high intensity peak which appears at 72 874 cm\(^{-1}\) (see Fig. 4).

All in all, the analyses allowed assignment of the Rydberg state spectra with respect to \( n, l, \lambda \) and \( \nu' \) as well as determination of band origin \( (\nu_0^l) \), vibrational wavenumber \( (\omega_a) \), and in some cases anharmonicity constants \( (\omega_a x_a) \) for the Rydberg states (see Tables 1 and 2).

**Ion pair threshold energetics**

Close-up figure in the threshold energy region reveals missing vibrational bands below 72 020 cm\(^{-1}\) (Fig. 4b). The lack of observable lines in that region must correspond to transitions with energy levels below the ion pair dissociation energy threshold for I₂. The Active Thermochemical Tables (ATcT) value of the ion pair production threshold is 862.0575 ± 0.0061 kJ mol\(^{-1}\) or 72 062.4 ± 0.5 cm\(^{-1}\), which is significantly larger than the observed cut off in our cipp spectra (≤72 030 cm\(^{-1}\)). This must be due to a shifting of the ion pair production threshold by the applied electric field in the extraction region of the spectrometer. The ion pair production threshold is known to red-shift in energy \( (\Delta E) \) proportionally to the square root of the electric field \( (E) \) as,

\[
\Delta E = z\sqrt{F}
\]

were \( z \) is the shift constant.28–31 Typical measured values of \( z \) range from −3.9 to −6.11 cm\(^{-1}\), when \( F \) is given in V cm\(^{-1}\).

The relative intensity of the spectral band at 72 025 cm\(^{-1}\) is found to increase with the electric field \( (F) \) (see Fig. 1 and 5). This can be attributed to a different cutoff of the rotational energy levels of the \( 7p(1/2) (\nu' = 3) \) vibrational Rydberg state, as the ion pair energy threshold decreases with increasing \( F \).
A good fit to the experimentally determined relative intensities in the 44.3 V cm\(^{-1}\) and 17.7 V cm\(^{-1}\) cipp spectra in the 72 015–72 080 cm\(^{-1}\) region was achieved when the spectral simulations were carried out with or without including transitions to the lowest 20\(J\) rotational energy levels, as shown in Fig. 5. Thus, by assigning the cutoff energy in the 17.7 V cm\(^{-1}\) cipp spectrum to the energy of the \(J = 20\) levels of the 7\(p\sigma(1/2)\) (\(v' = 3\)) state, a value of \(v = -5.5 \pm 0.2\) cm\(^{-1}\) was obtained for the \(I_2\) cipp process.

This observed field dependence is markedly different from what we saw in the \(F_2\) cipp experiments, where the rotational energy resolution allowed us to directly observe how the individual rotational lines exhibited energy-dependent Stark shifts, with the \(J = 5\) individual rotational lines exhibiting energy-dependent Stark shifts, with the \(J = 5\) energy range.

A magnified spectrum in the ion pair threshold energy region. Red broken line shows the ion pair threshold value (72 062.4 \pm 0.5 cm\(^{-1}\)).

IV. Discussion

As the excitation energy closes in on the ionization potential of molecules, discreet rotational and vibrational spectra structures can be difficult to obtain by spectroscopic means. This can be partly due to increasing overlap of spectral features in association with larger density of states as the energy increases, and partly due to enhanced line broadening in association with shorter lifetime of states as the number of decay pathways increase with energy. The nature of the coincidence ion pair detection using high-resolution synchrotron radiation in conjunction with a supersonic molecular beam source bypasses some of these problems. First, the technique allows a distinction between direct ion and ion pair formation and offers very low background noise, due to the coincidence detection. Second, the jet-cooling reduces the number of observable rotational and vibrational excitations and therefore lowers overlap of spectral features. Third, in addition to a photon absorption, a crossing from the excited states to ion-pair states is involved. Thus, the latter step acts selectively to detect only spectra of Rydberg states with non-zero probabilities for transfer to the ion-pair states.

Comparison of our results with an earlier work on excitation functions for \(I^+\) and \(I^-\) formed from photodissociation of \(I_2\) is of particular interest.\(^6\) The coincident ion pair detection method combined with a supersonic molecular beam inlet and a high-resolution photon source is found to greatly improve sensitivity, selectivity, and spectral resolution, allowing for detection of a many more Rydberg state transitions. The low-resolution excitation spectra in the observation region of concern were attributed to a minimum of 5 overlapping Rydberg state spectra. Three of these spectra were assigned to transitions to \([\sigma_{g}^{2} \pi_{u}^{2} \pi_{u}^{2} \pi_{g}]_{\Pi_{1/2u}}\) mpt Rydberg states for \(n = 9, 10,\) and 11 whereas others were left unassigned. Those analyses were based on quantum defect calculations and spectral simulations as well as an analogy to corresponding spectra derived for \(Br_2.\)\(^5\) In contrast, our analysis reveals the involvement of a total of fifty Rydberg states in that spectral region.

All Rydberg states observed are of ungerade symmetry and either \(\Omega = 0\) or 1 according to selection rules. Therefore, assuming that homogeneous state interactions (\(\Delta \Omega = 0\)) and conservation of the symmetry (\(u \leftrightarrow u\)) hold for the Rydberg to ion-pair state transfer process, only two (\(D(0_u)\) and \(\gamma(1_u)\)) of six possible ion-pair states (\(D(0_u), \gamma(1_u), \delta(2_u), E(0_u), \beta(1_u),\) and \(D'(2_u)\)) are involved.\(^3\) The Voigt profile line widths derived from our simulation calculations of about 9.1 cm\(^{-1}\) (see above) is close to the expected fwhm of cipp spectral peaks of about 1.2 meV/9.7 cm\(^{-1}\), suggesting that the lifetime of the Rydberg state is not shorter than about 0.6 ps.

V. Summary and conclusions

Coincidence ion pair detection was used for photoexcitation of jet cooled \(I_2\) molecular beam in the 71 940–74 000 cm\(^{-1}\) photon energy region. The observed peak structures were attributed to vibrational bands due to transitions from the ground state \(I_2\) \((X'\Sigma^+(v' = 0, 1))\) to a number of Rydberg states, followed by transfer to ion-pair states above the dissociation threshold to
Table 2  (a) Vibrational band origins \( \nu \) and vibrational constants \( \omega_{\nu} \), \( \omega_{\nu}' \), \( \omega_{\nu}'' \) for Rydberg states corresponding to electron transitions to p Rydberg orbitals which belong to series converging to the \( \Omega = 3/2 \) ground state of I2. (b) Vibrational band origins \( \nu \) and vibrational constants \( \omega_{\nu} \), \( \omega_{\nu}' \), \( \omega_{\nu}'' \) for Rydberg states corresponding to electron transitions to f Rydberg orbitals which belong to series converging to the \( \Omega = 3/2 \) ground state of I2. (c) Vibrational band origins \( \nu \) and vibrational constants \( \omega_{\nu} \), \( \omega_{\nu}' \), \( \omega_{\nu}'' \) for Rydberg states corresponding to electron transitions to p and f Rydberg orbitals which belong to series converging to the \( \Omega = 1/2 \) ground state of I2.

| Configuration | \( \nu \) [cm\(^{-1}\)] | \( \omega_{\nu} \) [cm\(^{-1}\)] | \( \omega_{\nu}' \) [cm\(^{-1}\)] | Relative intensity |
|---------------|-----------------|-----------------|-----------------|------------------|
| (a) \[ \sigma_{g}^{4} \pi_{u}^{4} \pi_{u}^{2} \sigma_{u}^{4} \Pi_{3/2} \] n\( \lambda \). | | | | |
| 9p\( \pi \)u | 71.350 | 241 | 0.8 | 0.50 |
| 10p\( \pi \)u | 72.416 | 240 | 0.6 | 0.10 |
| 11p\( \pi \)u | 73.086 | 240 | 0.6 | 0.10 |
| 12p\( \pi \)u | 73.522 | 240 | 0.6 | 0.30 |
| 9p\( \pi \)u | 71.389 | 239 | 0.4 | 0.25 |
| 10p\( \pi \)u | 72.440 | 239 | 0.8 | 0.50 |
| 11p\( \pi \)u | 73.098 | 241 | 0.6 | 0.20 |
| 12p\( \pi \)u | 73.535 | 241 | 0.6 | 0.20 |
| 9p\( \pi \)u | 71.485 | 196 | 0.1 | 0.70 |
| 10p\( \pi \)u | 72.496 | 206 | 0.2 | 0.40 |
| 11p\( \pi \)u | 73.138 | 199 | 0.6 | 0.35 |
| 12p\( \pi \)u | 73.563 | 205 | 0.6 | 0.4 |
| 9p\( \pi \)u | 71.654 | 190 | 0.4 | 0.20 |
| 10p\( \pi \)u | 72.602 | 190 | 0.2 | 0.25 |
| 11p\( \pi \)u | 73.200 | 190 | 0.4 | 0.2 |
| 12p\( \pi \)u | 73.608 | 190 | 0.6 | 0.2 |
| (b) \[ \sigma_{g}^{4} \pi_{u}^{4} \pi_{u}^{2} \sigma_{u}^{4} \Pi_{3/2} \] n\( \lambda \). | | | | |
| 7f\( \pi \)u | 72.000 | 242 | 0.6 | 0.3 |
| 8f\( \pi \)u | 72.815 | 239 | 0.6 | 0.25 |
| 9f\( \pi \)u | 73.341 | 240 | 0.6 | 0.1 |
| 10f\( \pi \)u | 73.705 | — | — | — |
| 7f\( \pi \)u | 72.035 | 230 | 0.2 | 0.8 |
| 8f\( \pi \)u | 72.839 | 231 | 0.6 | 0.4 |
| 9f\( \pi \)u | 73.360 | 231 | 0.6 | 0.2 |
| 10f\( \pi \)u | 73.719 | — | — | — |
| 7f\( \pi \)u | 72.054 | 217 | 0.5 | 0.8 |
| 8f\( \pi \)u | 72.850 | 215 | 0.6 | 0.4 |
| 9f\( \pi \)u | 73.368 | 216 | 0.6 | 0.2 |
| 10f\( \pi \)u | 73.724 | — | — | — |
| 7f\( \pi \)u | 72.135 | 224 | 0.8 | 0.23 |
| 8f\( \pi \)u | 72.901 | 223 | 0.8 | 0.2 |
| 9f\( \pi \)u | 73.403 | 222 | 0.6 | 0.5 |
| 10f\( \pi \)u | 73.748 | — | — | — |
| 7f\( \pi \)u | 72.155 | 237 | 0.2 | 0.8 |
| 8f\( \pi \)u | 72.914 | 238 | 0.2 | 0.4 |
| 9f\( \pi \)u | 73.409 | 239 | 0.6 | 0.3 |
| 10f\( \pi \)u | 73.750 | — | — | — |
| 7f\( \pi \)u | 72.175 | 214 | 0.5 | 0.4 |
| 8f\( \pi \)u | 72.930 | 216 | 0.6 | 0.35 |
| 9f\( \pi \)u | 73.422 | 218 | 0.3 | 0.2 |
| 10f\( \pi \)u | 73.766 | — | — | — |

| \[ \sigma_{g}^{4} \pi_{u}^{4} \pi_{u}^{2} \sigma_{u}^{4} \Pi_{1/2} \] n\( \lambda \). | | | | |
| 7p\( \pi \)u | 70.930 | 238 | 0.9 | 0.5 |
| 7p\( \pi \)u | 71.085 | 237 | 0.8 | 0.35 |
| 7p\( \pi \)u | 71.449 | 196 | 0.4 | 0.4 |
| 7p\( \pi \)u | 72.096 | 190 | 0.8 | 0.25 |
| 5f\( \pi \)u | 73.319 | 238 | 0.6 | 0.2 |
| 5f\( \pi \)u | 73.438 | 231 | 0.6 | 0.5 |
| 5f\( \pi \)u | 73.502 | 216 | 0.6 | 0.2 |
| 5f\( \pi \)u | 73.773 | — | — | — |
| 5f\( \pi \)u | 73.901 | — | — | — |
| 5f\( \pi \)u | 73.912 | — | — | — |

\( ^{a} \) Based on simulation of spectra.

**Conflicts of interest**

There are no conflicts to declare.
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