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Resonance enhanced multiphoton ionization spectroscopy of carbon disulphide

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Rydberg excited states of the CS$_2$ molecule in the energy range 56 000–81 000 cm$^{-1}$ have been further investigated via the two and three photon resonance enhancements they provide in the mass resolved multiphoton ionization (MPI) spectrum of a jet-cooled sample of the parent molecule. Spectral interpretation has been aided by parallel measurements of the kinetic energies of the photoelectrons that accompany the various MPI resonances. Thus we have been able to extend, and clarify, previous analyses of the tangled spin–orbit split vibronic structure associated with the $^3\Pi_u$ and $^1\Pi_u$ states derived from the configuration [2$\Pi_g$]4$p\sigma_u$ and the $^3\Delta_u$, $^3\Sigma_u^+$, and $^1\Sigma_u^+$ states resulting from the configuration [2$\Pi_g$]4$p\pi_u$, and to deduce an approximate wave number for the origin of the hitherto unidentified $^3\Sigma_u^-$ state derived from this same configuration. Moving to higher energies we are able to locate, unambiguously, the origins of the next $(n=5)$ members of four of these [2$\Pi_g$]np Rydberg series, and to identify extensive series based on the presumed Rydberg configurations [2$\Pi_g$]n$s\sigma_u$ and [2$\Pi_g$]n$p\lambda_u$ with, in both cases, $n \approx 10$. We also identify MPI resonances attributable to CS($^3\Pi$) fragments, to ground state C atoms, and to S atoms in both their ground ($^3\Pi$) and excited ($^1S$) electronic states. Analysis of the former resonances indicates that the CS($^3\Pi$) fragments resulting from two photon dissociation of CS$_2$ at excitation wavelengths around 300 nm are formed with substantial rovibrational excitation.

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INTRODUCTION

Both the spectroscopy$^{1-16}$ and the photochemistry$^{9,17-30}$ of excited electronic states of the carbon disulphide molecule, CS$_2$, have been the subject of extensive study over the past half century. Like carbon dioxide, CS$_2$ has a linear ($D_{\infty h}$ symmetry) ground state geometry, with 16 valence electrons arranged in the configuration

$$\cdots (5\sigma_g)^2(4\sigma_u)^2(6\sigma_g)^2(5\sigma_u)^2(2\pi_u)^4(2\pi_g)^4;\tilde{X}^1\Sigma_g^+ (1)$$

with the highest occupied $2\pi_g$ orbital being largely non-bonding in character, and with the bulk of its associated electron density located on the terminal sulphur atoms. The molecule has three fundamental modes of vibrational motion: $v_1$, the symmetric stretch (which transforms as $\sigma_g^+$), $v_2$, the degenerate bend ($\pi_u$), and $v_3$, the asymmetric stretch ($\sigma_u^-$), the ground state frequencies of which are 658, 396, and 1535 cm$^{-1}$, respectively.$^4$

The $\tilde{X}^1\Pi_g$ ground state of the CS$_2^+$ ion is formed by removing an electron from the $2\pi_g$ orbital. It, too, has a linear equilibrium geometry. This ionic state is split into two spin–orbit components, of which the $^3\Pi_g$ state is lower in energy. High resolution photoelectron spectroscopy (PES)$^{31-33}$ and, particularly, recent zero kinetic energy (ZEKE) photoelectron studies$^{34}$ have established a value of 81 286±5 cm$^{-1}$ for this lowest ionization limit, a spin–orbit splitting of 440 cm$^{-1}$, and vibrational frequencies of ca. 620, 332, and 1195 cm$^{-1}$ for, respectively, the $v_1$, $v_2$, and $v_3$ normal modes in the ground state ion. The present study is solely concerned with Rydberg states belonging to series that converge to one or other spin–orbit component of the ground state ion.

The literature contains many reports of studies of the ultraviolet (uv) and vacuum ultraviolet (vuv) absorption spectrum of CS$_2$. The 290–410 nm region contains a wealth of resolved rovibronic structure, much of which has now been assigned$^{2,6,7,12,16}$ in terms of excitations to the so-called $R, S, U, V$, and $T$ states—bent valence states arising as a result of the electronic promotion $3\pi_u^-\rightarrow 2\pi_g^-$. Proceeding to shorter wavelengths, the next feature of note is a reasonably intense vibronic progression spanning the region 190–210 nm; the partial analyses reported to date$^3$ are consistent with this being associated with excitation to the bent $^1B_2$ component of the $^1\Sigma_u^+(3\pi_u^-\rightarrow 2\pi_g^-)$ state. Price and Simpson$^1$ were the first to identify two Rydberg series in the vuv region, converging to the two spin–orbit components of the ground state ion.

The energy range up to and including the first ionization limit has been much studied subsequently, both in one photon absorption$^{5,8,13,14}$ and by electron impact spectroscopy,$^{10,11}$ but multiphoton studies of the excited states of CS$_2$, have, until very recently, remained sparse. Yet, as we are reminded in Table I, it is for centrosymmetric systems like CS$_2$ that multiphoton studies should, potentially at least, be most valuable.$^{35}$ Indeed, the only Rydberg states for which a one photon electric dipole excitation from the
TABLE I. Orbital and upper state symmetries accessible by one, two, and three photon induced transitions from the \( \sim (2\pi)^4 \times \Sigma_g^+ \) ground state. Only those upper states which can be reached on the basis of molecular selection rules are included.

<table>
<thead>
<tr>
<th>Number of photons</th>
<th>Orbital type</th>
<th>Orbital symmetry</th>
<th>Upper state symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( p )</td>
<td>( \sigma_u )</td>
<td>( \Pi_u )</td>
</tr>
<tr>
<td></td>
<td>( s )</td>
<td>( \pi_u )</td>
<td>( \Sigma_g^+ )</td>
</tr>
<tr>
<td></td>
<td>( d )</td>
<td>( \sigma_g )</td>
<td>( \Pi_g )</td>
</tr>
<tr>
<td>2</td>
<td>( p )</td>
<td>( \sigma_u )</td>
<td>( \Pi_u )</td>
</tr>
<tr>
<td></td>
<td>( f )</td>
<td>( \sigma_u )</td>
<td>( \Pi_u )</td>
</tr>
</tbody>
</table>

Ground \( (\Sigma_g^+) \) state should be fully allowed are those derived from the configurations involving the \( ^2\Pi \) ion core and an ungerade (e.g., \( p \) or \( f \)) Rydberg electron; it is generally accepted that the dominant series observed in the early absorption work\(^3\) is associated with the \( [^2\Pi_g]np\sigma_g \) configuration. Two photon excitations, in contrast, should offer the possibility of populating Rydberg states involving gerade Rydberg orbitals, e.g., those associated with the configurations \( [^2\Pi_g]n\sigma_g \), \( [^2\Pi_g]n\pi_g \), \( [^2\Pi_g]n\delta_g \), and \( [^2\Pi_g]n\phi_g \), while population of additional high angular momentum Rydberg states derived from the configuration \( [^2\Pi_g]n\lambda_g \) might be anticipated in three photon excitation spectroscopy. This is the motivation behind the present study.

For completeness, we here summarize the still somewhat fragmentary conclusions of the multiphoton studies of \( \text{CS}_2 \) reported thus far. Couris et al.\(^36\) have reported a 2+1 resonance enhanced multiphoton ionization (REMPI) study of the 54 000–58 000 cm\(^{-1}\) energy region and identified resonances due to the two states (derived from the two spin–orbit states of the ion core) associated with the excited configuration \( [^2\Pi_g]4\sigma_g \). Li et al.\(^37,38\) and, more recently, Baker and co-workers\(^39,40\) have investigated the energy range 62 000–65 000 cm\(^{-1}\) using both one color 3+1 and two color (1+1+1)+1 REMPI spectroscopy. As a result it is now clear that, in this energy range, the vertical electronic spectrum of \( \text{CS}_2 \) is dominated by transitions to excited states derived from the Rydberg configuration \( [^2\Pi_g]4\rho \lambda_u \). As we show later, the present REMPI studies, supplemented by parallel measurements of the accompanying REMPI-PE spectra, serve to substantiate, and refine, many of the arguments contained in the latter works.\(^39,40\)

Assignments proposed in a number of the earlier studies\(^3,5,8\) of the Rydberg states of \( \text{CS}_2 \) have been based on analogy with the all-first-row prototype \( \text{CO}_2 \), for which a number of rotationally resolved Rydberg transitions are known and for which a limited range of \textit{ab initio} calculations have been reported.\(^41\) In the context of the present work it is pertinent to note that recent 3+1 REMPI and REMPI-PES studies of \( \text{CO}_2 \) have revealed the spin–orbit split \( [^2\Pi_g]3\rho \sigma_u \)

Rydberg state and a series of spin–orbit split resonances associated with the configuration \( [^2\Pi_g]n\rho \lambda_u (n = 4–13) \).\(^42–47\) Higher members of the \( p \) Rydberg series were not observed, presumably because these excited states are heavily predissociated.\(^46\) Excited states of the noncentrosymmetric analog \( \text{OCS} \) in the energy region 70 000–76 000 cm\(^{-1}\) have also been investigated by REMPI spectroscopy,\(^46–50\) but because of its lower \( (C_{\nu s}) \) symmetry, there is no \( u/g \) parity selection rule and the parallels with \( \text{CO}_2 \) and \( \text{CS}_2 \) are expected to be less marked.

Here, we report the first comprehensive study of the entire two and three photon REMPI spectra of a jet-cooled sample of carbon disulphide up to the first ionization limit. Numerous vibronic features are apparent in each spectrum and many of these resonances can be assigned as members of well defined Rydberg series converging to the two spin–orbit components of the ground state of the molecular ion. As in the recent REMPI study of \( \text{CO}_2 \),\(^46\) definitive interpretation of the individual vibronic features appearing in these spectra has been greatly aided by concurrent measurements of the kinetic energies of the photoelectrons accompanying the REMPI process.

**EXPERIMENT**

The results reported here were obtained using two complementary experimental setups: In Bristol, a home-built time-of-flight (TOF) mass spectrometer was used to record mass resolved REMPI spectra of \( \text{CS}_2 \), and in Amsterdam REMPI-PES studies were performed using a “magnetic bottle” spectrometer. Both experiments have been described in detail previously\(^51–54\) so only brief summaries of the two experimental methods are given here.

REMPI spectra were recorded using a pulsed nozzle to inject samples of \( \text{CS}_2 \) (either as a 10% mixture diluted in argon to a total pressure of ca. 1 atm, or as the pure gas) into the source region of the TOF mass spectrometer. The gas pulses were crossed by the focused (f.l. = 200–300 mm) output of a tuneable Nd:YAG pumped dye laser, which was frequency doubled when necessary. Wavelength calibration of the dye laser, in the visible, was performed simultaneously with recording of REMPI spectra by measurement of the optogalvanic spectrum of neon excited in a hollow cathode discharge. Ions formed by the focused laser beam in the mass spectrometer were subjected to two stages of acceleration prior to entering a field-free drift region and were detected by a channel electron multiplier (channeltron). The amplified output of the channeltron was monitored using a digital oscilloscope connected to a PC via an IEEE interface. To obtain mass selected REMPI spectra, the dye laser was scanned and only that part of the total ion signal that fell within a narrow time window centered on the TOF of the mass of interest was collected, averaged, and stored.

REMPI-PE spectra were obtained using an excimer pumped dye laser system with the laser output being frequency doubled when required and focused (f.l. = 25 mm) into the ionization region of the magnetic bottle electron spectrometer. An effusive beam of pure \( \text{CS}_2 \) vapor was
crossed by the focused laser beam and photoelectrons resulting from each laser pulse were extracted into the spectrometer. The measured times of arrival of the photoelectrons at a pair of microchannel plates situated at the end of the 500 mm flight tube were used to determine electron kinetic energies. A transient digitizer, interfaced to a PC, recorded preamplified output signals from the microchannel plates. Certain wavelength-resolved REMPI spectra were recorded in Amsterdam by measuring the total photoelectron yield as a function of excitation wavelength. Kinetic-energy-resolved photoelectron spectra were obtained by progressively stepping the retarding voltage on a grid in the flight tube and, at each voltage setting, producing electron spectra were obtained by progressively stepping the time-to-energy transformation of excitation wavelength. Kinetic-energy-resolved photon-electron spectra were obtained by progressively stepping the wavelength on a grid in the flight tube and, at each wavelength setting, monitoring just the parent ion peak of only those ions with TOFs appropriate to m/2 60. This spectrum is a composite, obtained by splicing together spectra recorded using a number of different dyes. As discussed in the text, it was not possible to ensure correct normalization of the relative intensities of features appearing within the tuning range of any one dye, or between one dye tuning curve and the next. The vertical arrows arranged below the respective spectra indicate where the various scans have been joined. The n = 4 members of the various [2Π]np­ → ← 3Σu+ Rydberg series identified in Table I are indicated via the combs superimposed above the spectrum. The numbers above the various features (5a, 5b, etc.) refer to the photoelectron spectra recorded on these peaks and displayed in Figs. 5 and 6.

RESULTS AND DISCUSSION

REMPI Spectra

Figures 1 and 2 show the REMPI spectrum of CS2, resonance enhanced at the three photon energy, recorded using linearly polarized light and monitoring the total yield of photoelectrons. As with Fig. 1, this spectrum is a composite obtained by splicing together spectra recorded using a number of different dyes, and the same comments apply. Members of the various [2Π]np­ → ← 3Σu+ Rydberg series and the [2Π]nf­ → ← 1Σg+ complexes identified in Tables I and II are indicated via the combs and brackets festooned above the spectrum. The peaks identified by the symbols * and † indicate atomic carbon and atomic sulphur resonances, respectively.

Fig. 1. 3+1 REMPI spectrum of a jet-cooled sample of CS2 over the energy range 60 840–81 000 cm−1 recorded using linearly polarized light and monitoring only those ions with TOFs appropriate to m/2 60. This spectrum is a composite, obtained by splicing together spectra recorded using a number of different dyes. As discussed in the text, it was not possible to ensure correct normalization of the relative intensities of features appearing within the tuning range of any one dye, or between one dye tuning curve and the next. The vertical arrows arranged below the respective spectra indicate where the various scans have been joined. The n = 4 members of the various [2Π]np­ → ← 3Σu+ Rydberg series identified in Table I are indicated via the combs superimposed above the spectrum. The numbers above the various features (5a, 5b, etc.) refer to the photoelectron spectra recorded on these peaks and displayed in Figs. 5 and 6.

Fig. 2. 3+1 REMPI spectrum of a near room temperature sample of CS2 over the energy range 68 400–81 000 cm−1 recorded using linearly polarized light and monitoring the total yield of photoelectrons. As with Fig. 1, this spectrum is a composite obtained by splicing together spectra recorded using a number of different dyes, and the same comments apply. Members of the various [2Π]np­ → ← 3Σu+ Rydberg series and the [2Π]nf­ → ← 1Σg+ complexes identified in Tables I and II are indicated via the combs and brackets festooned above the spectrum. The peaks identified by the symbols * and † indicate atomic carbon and atomic sulphur resonances, respectively.
64 209 cm$^{-1}$ (64 214 cm$^{-1}$ in Ref. 39) feature simply because, at the relevant excitation frequencies, an accidental one photon resonance in the CS$_2^+$ parent ion greatly enhances its probability of undergoing two photon dissociation (as evidenced by a dramatic increase in the S$^+$ and CS$^+$ fragment ion yields). The small shoulders evident on the high mass side of each of the major sulphur containing ions in Fig. 4 are due to the presence of the $^{34}$S isotope; the finite TOF resolution at these higher ion masses, allied with the weakness of these features, prevented us from recording any worthwhile REMPI spectra associated with the heavier isotopomers. With the exception of the S$_2$ species, all of the other fragments were seen to exhibit some spectrosopy of their own: This we discuss later.

**Photoelectron spectra**

The kinetic energy resolution of the present REMPI-PES measurements (ca. 15 meV) is more than sufficient for us to be able to distinguish ionizations to the $^2\Sigma_g^+$ and $^2\Pi_g$ spin–orbit components of the ground state ion (2 Å≈440 cm$^{-1}$, 54.6 meV)$^{34}$ For simplicity, these will henceforth be referred to simply as [3/2] and [1/2], respectively; when appropriate, these labels will also be used to indicate the ion

![Figure 3](https://example.com/fig3.png)

![Figure 4](https://example.com/fig4.png)
core involved in the various Rydberg states. Representative sets of REMPI-PE spectra are shown in Figs. 5–7 and will be considered in turn. The PE spectra shown in Fig. 5 all arise as a result of three photon resonant, four photon ionization processes. The first two both show one dominant peak, consistent with the final one photon ionization step from the resonance enhancing Rydberg state involving a $\Delta v=0$ transition (as expected on Franck-Condon grounds if the Rydberg state has a very similar geometry to that of the ion) to predominantly one of the two spin–orbit states of the ion. The first PE spectrum [Fig. 5(a)] was obtained following excitation at 483.1 nm ($3\nu=62\,100\,\text{cm}^{-1}$); the kinetic energy of the major peak (0.188 eV) is consistent with ionization to the $v^+=0$ (shorthand notation for $v_1^+=v_2^+=v_3^+=0$) level of the lower, [3/2], spin–orbit component of the ion thus implying, by Franck-Condon arguments, that the resonance enhancement also involves an electronic origin, almost certainly that of a Rydberg state built on the [3/2] ion core. Such a conclusion is fully consistent with that reached in a number of previous analyses;8,10,13,39 namely, that this feature should be assigned as the origin of the $[3/2]4p\pi_u(3\Pi_u^o)-X^2\Sigma_g^+$ Rydberg transition. By way of contrast, Fig. 5(b) shows the complementary REMPI-PE spectrum that results when we excite at 467.2 nm ($3\nu=64\,209\,\text{cm}^{-1}$), via the origin of a Rydberg state involving the [1/2] core. The measured photoelectron kinetic energies indicate that the resulting ions are formed in the $v^+=0$ level of the [1/2] spin–orbit state of the ion, thereby serving to confirm the recent assignment of this feature as the origin of the $[1/2]4p\pi_u(3\Delta_u^o)-X^2\Sigma_g^+$ Rydberg transition.39,40

Not all of the resonance enhancing levels ionize so “cleanly” as those shown in Figs. 5(a) and 5(b). Consider, for example, the features appearing at 471.4 and 471.0 nm ($3\nu=63\,644$ and $63\,700\,\text{cm}^{-1}$, respectively), both of which have at various times39,40 been assigned as the lower energy $[3/2]4p\pi_u(3\Delta_u^o)-X^2\Sigma_g^+$ counterpart of the 64 209 cm$^{-1}$ resonance. The associated REMPI-PE spectra shown in Figs. 5(c) and 5(d) suggest a solution to the existing ambiguity. The former shows four peaks, the largest, fastest of which duly appears at a kinetic energy (0.443 eV) consistent with ionization to the [3/2], $v^+=0$ level of the ion. Ionization to the [1/2], $v^+=0$ level is seen to occur with only low probability, again consistent with the premise that the intermediate Rydberg state does indeed have a reasonably pure [3/2] ion core. What then should we make of the two additional peaks at 0.360 and 0.306 eV which, on energetic grounds, we associate with formation of ions with both [3/2] and [1/2] cores, each with ca. 650 cm$^{-1}$ of internal energy? The photoelectron spectrum resulting from 3+1 REMPI via the neighboring 63 700 cm$^{-1}$ feature [Fig. 5(d)] exhibits the same peaks, but the relative intensities of the “fast” and “slow” kinetic energy peaks are reversed. The obvious explanation, upon which we elaborate further in the later discussion, is that these two resonances are the result of vibronic mixing between two levels which, in zero order, should be viewed as (i) an electronic origin involving the [3/2] ion core and (ii) an excited level (carrying some 650 cm$^{-1}$ of vibrational energy) built on a spin–orbit “mixed” core. Our final example in this panel [Fig. 5(e)] shows a further example of ionization from an intermediate state which appears to be built on a mixed ion core. This photoelectron spectrum was obtained following 3+1 REMPI at an excitation wavelength of 466.1 nm ($3\nu=64\,369\,\text{cm}^{-1}$), a feature that has been tentatively assigned39 as the origin of the $1\Sigma_g^+\leftarrow X^2\Sigma_g^+$ transition associated with the $4p\pi_u\leftarrow 2\pi_g$ Rydberg excitation. It is dominated by peaks indicative of ion formation in the $v^+=0$ levels of both spin–orbit states of the ion.

Figure 6 shows further examples of the way in which REMPI-PEs can aid the assignment of individual vibronic features observed in the wavelength resolved REMPI spectra. Consider the three photon resonance evident in Fig. 1 at an excitation wavelength of 478.3 nm ($3\nu=62\,720\,\text{cm}^{-1}$). Should we assign this as a transition involving a vibrationally excited level of the Rydberg state with origin at 62 100 cm$^{-1}$, carrying ca. 620 cm$^{-1}$ of internal energy, or as a “hot band” associated with the Rydberg state at 62 780 cm$^{-1}$ (see Table II)? Analysis of the corresponding REMPI-PE spectrum [shown in Fig. 6(a)] helps to clarify the situation. The strongest peak in this photoelectron spectrum appears at a kinetic energy ca. 650 cm$^{-1}$ lower than that associated with formation of the vibrationless [3/2] ground state ion, thus supporting the suggestion that the three photon resonance is indeed associated with a vibrationally excited level (1$^1$) of the Rydberg state whose origin occurs at 62 100 cm$^{-1}$. This explanation, however, does not account for the other significant peak appearing in Fig. 6(a), at a kinetic energy of 0.238 eV, just where we might expect to observe any $\Delta v=0$ ionizations to the [1/2] spin–orbit state of the ion. Thus we are able to confirm the recent suggestion39 that the 62 720 cm$^{-1}$ feature actually consists of two overlapping transitions (see Table II), one of which involves the $v_1=1$ level of the Rydberg state whose origin appears at 62 100 cm$^{-1}$, the other a hot band, most probably the $2_1^1$ band (both on Boltzmann grounds and on the basis of the change in vibrational frequency upon exciting from the ground to the Rydberg state) of the Rydberg transition whose origin falls at 62 780 cm$^{-1}$.

Interpretation of the REMPI-PE spectra shown in Figs. 6(b) and 6(c), obtained following 3+1 REMPI at wavelengths of 463.5 and 453.7 nm ($3\nu=64\,724$ and 66 119 cm$^{-1}$, respectively), is less clear cut. In both cases the peaks corresponding to formation of $v^+=0$ ions are weak. The dominant feature in the former spectrum is a doublet, the kinetic energies of which (0.496 and 0.480 eV) are most readily interpretable in terms of formation of ions in their upper [1/2] spin–orbit state with ca. 590 and 710 cm$^{-1}$ of internal energy. Additional, yet higher resolution REMPI-PEs experiments will probably be needed in order to decide whether these internal energies should be associated with the formation of ions in one or more of the various Renner–Teller components associated with $v_1^+=2$ and/or with $v_1^+=1$. The dominant feature in Fig. 6(c) appears at a kinetic energy ca. 0.550 eV, some 243 meV (ca. 1960 cm$^{-1}$) below that of the peak associated with the formation of ions in their [1/2] spin–orbit state. The satellite feature at 0.608 eV shows...
a similar energy shift from the peak we associate with ionization to the origin level of the $\frac{3}{2}$ spin–orbit state of the ion. Such observations would be explicable if we assign the 66 119 cm$^{-1}$ resonance in terms of excitation to a vibrationally excited level of a Rydberg state built predominantly on the $[1\frac{1}{2}]$ ion core. The vibrational energy in the ion (1960 cm$^{-1}$) is most readily interpretable as three quanta of the symmetric stretching mode $v_1$. We note that the 66 119 cm$^{-1}$ feature in Fig. 1 exhibits a similar shift from the intense band at 64 209 cm$^{-1}$ [the associated REMPI-PE spectrum for which was featured in Fig. 5(b)]. It is thus tempting to assign the former resonance as the $1^3_0$ vibronic band associated with the Rydberg transition whose origin appears at 64 209 cm$^{-1}$ (see Table II), but inspection of either Fig. 1 or the entries included in Table II leaves some concerns as to the location of the corresponding $1^3_0$ and $1^5_0$ bands.

Our final two examples of REMPI-PE spectra are displayed in Fig. 7. These two spectra were obtained following excitation at 355.2 nm ($\tilde{\nu}$=56 965 cm$^{-1}$), respectively. Both excitations are consistent with two photon resonant, three photon ionization processes and were assigned as, respectively, the $[3\frac{1}{2}]$ and $[1\frac{1}{2}]$ Rydberg origins in the earlier $2+1$ REMPI study of Couris et al. At first sight, the complexity of their associated REMPI-PE spectra might cause one to doubt such assignments but, in fact, the present work confirms that these resonances are, indeed, Rydberg origin bands. The explanation for the apparent complexity of the REMPI-PE spectra rests on a chance coincidence between the energy separation of these two resonances (653 cm$^{-1}$) and the wave number of the symmetric stretching vibration, $v_1$ (~640 cm$^{-1}$ in the ground and Rydberg states of the neutral, and in the ground state of the ion). Consider first the photoelectron spectrum accompanying $2+1$ REMPI of CS$_2$ at 355.2 nm [Fig. 7(a)]. As the supporting energy level diagram illustrates, peaks $b$ and $a$ are consistent with two photon excitation from the ground state to the $[3\frac{1}{2}]$ Rydberg origin, followed by a further one photon ionization to the zero-point vibrational levels of both the $[3\frac{1}{2}]$ and $[1\frac{1}{2}]$. 

| Table II. Wave numbers, effective quantum numbers ($n^*$) and proposed assignments for observed molecular CS$_2$ three-photon resonances to the $[\frac{3}{2}]$ spin–orbit states. Values in parentheses correspond to the measurements of Baker et al. (Ref. 39). |
|---|---|---|
| $\frac{3}{2}\mu_{\sigma_+}(3\Pi_g)$ | $\frac{3}{2}\mu_{\sigma_+}(3\Pi_u)$ |
| $n^*$ | $n^*$ |
| $\tilde{\nu}$ (cm$^{-1}$) | Vibronic assignment | $\tilde{\nu}$ (cm$^{-1}$) | Vibronic assignment |
| 62 039 | (62 013) | $2^1_1$ | 62 563 | $2^1_1$ |
| 62 100 | (62 083) | Origin | 2.39 | 62 720 | (62 704) | $2^1_1$ |
| 62 720 | | $1^3_0$ | 62 780 | (62 768) | Origin | 2.40 |
| 71 694 | | Origin | 3.38 | 63 358 | (63 352) | $2^1_1$ |
| 63 424 | (63 413) | $1^5_0$ | 63 495 | $2^3_0$ |
| 72 168 | | Origin | 3.47 | 64 130 | | $2^1_1$ |
| 72 666 | | Origin | 3.48 | 64 209 | | Origin | 2.50 |
| 73 287 | | $1^3_0$ | 65 757 | $2^1_1$ |
| 66 119 | | $1^3_0$ | 66 119 | $1^3_0$ |
| 64 280 | (64 284) | $1^3_0$ | 66 280 | $1^3_0$ |
| 63 544 | (63 534) | $2^1_1$ | 66 369 | (64 374) | Origin | 2.55 |
| 63 578 | (63 578) | $2^1_1$ | 66 991 | (64 965) | Origin | 2.55 |
| 63 644 | (63 641) | Origin | 2.49 | 65 050 | $2^3_0$ |
| 64 280 | (64 284) | | 65 763 | $2^3_0$ |

---

spin–orbit states of the ion, thus implying that the ion core involved in this particular Rydberg state may be less “pure” than indicated by the state label used here. To account for the faster peaks \(d\) and \(e\) in Fig. 7(a), with kinetic energies of 0.475 and 0.419 eV, respectively, it is necessary to invoke a hot band transition, namely, two photon excitation from the \(v_1=1\) level of the ground state to the \([1/2]4s\sigma_g\) Rydberg origin (which because of the accidental near degeneracy is likely to be overlapped by, and quite possible mixed with, the \([3/2]4s\sigma_g, v_1=1\) level), followed by ionization terminating on the same zero-point levels of the ion. Note that, because of this accidental degeneracy and given the resolution of the present REMPI-PES experiments, any one photon ionization from the \([3/2]4s\sigma_g, v_1=1\) level terminating on the \(v_1^+=1\) levels of the ion (which, on Franck–Condon grounds, would be expected to be quite significant) will simply reinforce peaks \(a\) and \(b\). The 2+1 REMPI-PE spectrum taken at 351.1 nm [Fig. 7(b)] provides further evidence of the accidental degeneracy between the \([3/2]4s\sigma_g, v_1=1\) and \([1/2]4s\sigma_g, v=0\) levels of CS\(_2\). In this case, the initial two photon excitation is from the ground vibrational level to the overlapping and/or mixed \([1/2]4s\sigma_g, v=0\) and \([3/2]4s\sigma_g, v_1=1\) Rydberg levels; the main peaks evident in the REMPI-PE spectrum are consistent with ion formation in the \(v^+=0\) (peaks \(h\) and \(e\)) and \(v_1^+=1\) levels (peaks \(f\) and \(g\)) of both spin–orbit states of the ground state ion.

FIG. 5. Illustrative REMPI-PE spectra of CS\(_2\) obtained following excitation at (a) 483.1 nm, where we excite a three photon resonance (3\(\tilde{v}=62100\) cm\(^{-1}\)) involving the zero-point level of the \([3/2]4\rho\pi_u, (^3\Pi_u)\) Rydberg state, (b) 467.2 nm (3\(\tilde{v}=64209\) cm\(^{-1}\)), where the resonance enhancement is provided by the \([1/2]4\rho\pi_u, (^1\Delta_u)\) Rydberg origin and the kinetic energy of the dominant photoelectron peak indicates that the partner ion is formed in the ground \((v'=0)\) level of the upper \([1/2]\) spin–orbit state; (c) 471.4 nm (3\(\tilde{v}=63644\) cm\(^{-1}\)) and (d) 471.0 nm (3\(\tilde{v}=63700\) cm\(^{-1}\))—resonances which we attribute to the result of vibronic mixing between two states which, in zero-order, would be described as the \([3/2]4\rho\pi_u, (^1\Delta_u)\) Rydberg origin and the \(\Delta\) component of the \(2^1\) vibrational level associated with the \([3/2]4\rho\pi_u, (^3\Sigma_u^+)\) state—see the text for further details; (e) 466.1 nm (3\(\tilde{v}=64369\) cm\(^{-1}\)) involving the \([1/2]4\rho\pi_u, (^3\Sigma_u^+)\) origin level which shows ionization to both spin–orbit components of the ion. The kinetic energy scales have been offset so that the various vibronic states of the ion align vertically.

FIG. 6. MPI-PE spectra of CS\(_2\) obtained following excitation at (a) 478.3 nm (3\(\tilde{v}=62720\) cm\(^{-1}\)). On the basis of the measured photoelectron kinetic energies we deduce this three photon resonance to be a blend of two transitions; the \(1_2\) band of the \([3/2]4\rho\sigma_u, (^3\Pi_u)\)–\(\tilde{X}^1\Sigma_u^+\) Rydberg transition, and the \(2^1\) hot band of the corresponding \([1/2]4\rho\sigma_u, (^3\Pi_u)\)–\(\tilde{X}^1\Sigma_u^+\) excitation; (b) 463.5 nm (3\(\tilde{v}=64724\) cm\(^{-1}\)), where the kinetic energies of the dominant photoelectron peaks are consistent with the partner ion being formed in its \([1/2]\) spin–orbit state with ca. 590 and 710 cm\(^{-1}\) of vibrational energy; and (c) 453.7 nm (3\(\tilde{v}=66119\) cm\(^{-1}\)), where the kinetic energy of the dominant photoelectron peak is consistent with the partner ion being formed in its \([1/2]\) spin–orbit state with ca. 1960 cm\(^{-1}\) of vibrational energy. As in Fig. 5, the kinetic energy scales have been offset so that the various vibronic states of the ion align vertically.
Rydberg state belongs to a series converging to the @~. We generally choose to adopt a Hund’s case coupling scheme in which we explicitly separate the angular momenta of the ion core, whereas most previous workers have chosen to label these same excited states using the labels appropriated to a Russell–Saunders, or A, S, coupling scheme, viz., 3II and 1I. In what, at first glance, might appear to be just the two spin–orbit components of the 2II and 2I, Rydberg origin at (a) 355.2 nm (2ω=56 312 cm⁻¹) and (b) 351.1 nm (2ω=56 965 cm⁻¹). The accompanying schematic energy level diagrams provide an explanation for the unexpectedly complex appearance of these two REMPI-PE spectra. (See the text for further details.)

Assigning the multiphoton resonances

Band maxima (ν) for the features identified in this work are listed in Tables II–IV together with, when appropriate, their quantum defect (δ) and/or the effective quantum number [(n*)=n–δ], where n is the principal quantum number] calculated using the relationship

\[ \nu = E_j - R(n^*)^2, \]

where \( E_j = 81 286 \) or 81 726 cm⁻¹ according to whether the Rydberg state belongs to a series converging to the [3/2] or [1/2] spin–orbit component of the ion, and \( R \) is the Rydberg constant (109 737 cm⁻¹). For completeness, we also list the major peaks identified in the recent multiphoton studies. 36–40

Before discussing and assigning the resonances observed in Figs. 1–3 we should consider one aspect of nomenclature, namely, the most appropriate labeling scheme for the various Rydberg states. Consider, for example, the Rydberg states derived from the configuration \( \cdots (2\sigma_j)^1 (4s\sigma_j)^1 \). In what follows we generally choose to adopt a Hund’s case (c) coupling scheme in which we explicitly separate the angular momentum of the ion core, \( \Omega_c = \frac{3}{2} \) or \( \frac{1}{2} \), from that of the Rydberg electron, whereas most previous workers have chosen to label these same excited states using the labels appropriated to a Russell–Saunders, or A, S, coupling scheme, viz., 3II and 1I. Figure 8 shows the correlation between these two limits, and highlights the fact that it is the relative magnitudes of the exchange energy, \( K \), and the spin–orbit coupling constant, \( A \), that determine which is the more appropriate. Clearly, in the limit of high \( n \), as \( K \) tends to zero and in the absence of any clearly resolved rotational fine structure, it must be most appropriate to use the Hund’s case (c) scheme adopted in this work.

We now turn to discuss the various spectral features observed in the present REMPI work. Recalling Table I we recognize that, by virtue of the fact that \( CS_2 \) is centrosymmetric, the present 3+1 and 2+1 REMPI spectra originating from the \( \tilde{X} \Sigma_g^+ \) ground state should provide complementary information (relating to, respectively, the ungerade and gerade excited states). For organizational simplicity we therefore choose to consider these two sets of transitions in turn.

### Table III: Observed molecular \( CS_2 \) three-photon resonances to the \( [\Pi_L]^e \) Rydberg states. The wave numbers given are for the center of each particular band. \( \Omega^+ \) represents the dominant ion core configuration as revealed by the REMPI-PE spectra.

<table>
<thead>
<tr>
<th>( \nu^+ (\text{cm}^{-1}) )</th>
<th>n</th>
<th>( \Omega^+ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>74 016</td>
<td>4</td>
<td>3/2</td>
</tr>
<tr>
<td>74 532</td>
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<tr>
<td>76 730</td>
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<td>3/2</td>
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<tr>
<td>77 160</td>
<td>5</td>
<td>3/2</td>
</tr>
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<td>78 144</td>
<td>6</td>
<td>3/2</td>
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<tr>
<td>78 570</td>
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<td>3/2</td>
</tr>
<tr>
<td>79 969</td>
<td>7</td>
<td>3/2</td>
</tr>
<tr>
<td>79 440</td>
<td>7</td>
<td>3/2</td>
</tr>
<tr>
<td>79 536</td>
<td>8</td>
<td>3/2</td>
</tr>
<tr>
<td>79 980</td>
<td>8</td>
<td>3/2</td>
</tr>
<tr>
<td>79 902</td>
<td>9</td>
<td>3/2</td>
</tr>
<tr>
<td>80 352</td>
<td>9</td>
<td>3/2</td>
</tr>
<tr>
<td>80 172</td>
<td>10</td>
<td>3/2</td>
</tr>
<tr>
<td>80 610</td>
<td>10</td>
<td>3/2</td>
</tr>
</tbody>
</table>

### Table IV: Wave numbers, principal quantum number (n), and vibronic assignments when not an electronic origin, and quantum defects (δ) for the presumed \( [\Pi_L]^e \) Rydberg states. The values in parentheses correspond to the measurements of Couris et al. (Ref. 36). Those positions indicated with an asterisk are very weak and only observable via electron detection (see Fig. 10).

<table>
<thead>
<tr>
<th>( \nu^+ (\text{cm}^{-1}) )</th>
<th>n</th>
<th>δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>( [3/2] \nu s \sigma_j (\Pi_L) \rightarrow \tilde{X} \Sigma_g^+ )</td>
<td>( \delta )</td>
<td></td>
</tr>
<tr>
<td>( 56 312 )</td>
<td>4</td>
<td>1.91</td>
</tr>
<tr>
<td>( 56 315 )</td>
<td>(56 974)</td>
<td></td>
</tr>
<tr>
<td>( 69 414 )</td>
<td>5</td>
<td>1.96</td>
</tr>
<tr>
<td>( 69 756 )</td>
<td>(69 847)</td>
<td></td>
</tr>
<tr>
<td>( 74 628 )</td>
<td>6</td>
<td>2(1)</td>
</tr>
<tr>
<td>( 74 701 )</td>
<td>6</td>
<td>2(1)</td>
</tr>
<tr>
<td>( 75 378 )</td>
<td>6</td>
<td>2(1)</td>
</tr>
<tr>
<td>( 75 965 )</td>
<td>6</td>
<td>2(1)</td>
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<td>( 76 998 )</td>
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<td>( 77 061 )</td>
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<td>2(1)</td>
</tr>
<tr>
<td>( 78 902 )</td>
<td>9</td>
<td>1.90</td>
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<tr>
<td>( 79 980 )</td>
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<td>( 80 352 )</td>
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<td>1.90</td>
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<td>( 80 172 )</td>
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<td>1.90</td>
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<tr>
<td>( 80 610 )</td>
<td>10</td>
<td>1.90</td>
</tr>
</tbody>
</table>
but this same group chose to assign the 62 100 cm \(^{-1}\), to absorption\(^5,8,13\) and the more recent REMPI studies, \(^{39,40}\) we
conclusions of several of the earlier one photon
has remained a matter of some controversy. Guided by sym-
tation as a hot band—a suggestion which the present
assignments in terms of transitions to excited levels of these gerade elec-
terms and, in this particular case, as Figs. 5(b) and 5(c)
showed, of disproving them. Both features correspond to
of electronic origin transitions, ionizing (predominantly) to the
the [3/2] and (cleanly) to the [1/2] states of the ion, respectively.
The quantum defects of the two features (\(\delta=1.5\), assuming
\(n=4\)) suggest that these are the first members of another \(p\)
Rydberg series, presumably ones based on the configuration
\([-\Pi_2]4p\,\pi_u\). Since these features have no obvious counter-
parts in the one photon absorption spectrum\(^{1,5,8}\), it is tempting
to suggest that they arise as a result of excitations to states with
\(\Omega_{total}>1\), most probably states which, in the language of
(\(\Lambda, S\)) coupling, would be described using the term symbols
\(3\Delta_u\) and \(1\Delta_u\). Baker and co-workers\(^{39,40}\) have reached
broadly similar conclusions, though the apparent splitting of
the origin at lower energy remained something of a puzzle.

These workers initially assigned the feature at 63 644 cm\(^{-1}\)
as the 2\(^1\) hot band of an electronic origin at 63 700 cm\(^{-1}\)
but this assignment was revised in their subsequent
two-color\(^{40}\) study in favor of an interpretation in which both
of these features were due to origin bands. As we have seen,
the present photoelectron spectra [Figs. 5(c) and 5(d)] sug-
gest that these two closely spaced features are best pictured
as arising from vibronic mixing between two zero-order
states, one of which is the [3/2]\(4p\,\pi_u\,\left(3\Delta_u\right)\) origin level,
while the other is built on a spin–orbit mixed core and
involves some 650 cm\(^{-1}\) of internal energy. Given the
expected energetic ordering of the various (\(\Lambda, S\)) states derived
from the configuration (\(2\pi_u\),\(3(4p\,\pi_u)\)–viz.,
\(1\Sigma_g^+,1\Delta_u,1\Sigma_u^+,3\Sigma_u^-,3\Delta_u\), and \(3\Sigma_u^+\), in order of decreasing
energy\(^{57}\)—and the fact that the two zero-order states must
have the same vibronic symmetry, we suggest the 2\(^1\) level of
the hitherto unobserved [3/2]\(4p\,\pi_u\,\left(3\Sigma_u^-\right)\) state as the most
plausible assignment for the other zero-order state, and that
this borrowing intensity from mixing with the
[3/2]\(4p\,\pi_u\,\left(3\Delta_u\right)\) origin level. Such an assignment implies a
term value ca. 63 050 cm\(^{-1}\) for the [3/2]\(4p\,\pi_u\,\left(3\Sigma_u^-\right)\) origin.
Core mixing appears to be a characteristic of the \(\Sigma_u\) members
of the [\(\Pi_u\)]4p\,\pi_u\] Rydberg complex: Recall that the photoelectron spectrum [Fig. 5(e)] obtained following 3+1
REMPI via the 64 369 cm\(^{-1}\) resonance which, in accord with
Baker et al.\(^{39,40}\) we assign as the origin of the
[3/2]\(4p\,\pi_u\,\left(3\Sigma_u^-\right)\) transitions, also showed clear evidence
for formation of \(v=0\) ions in both spin–orbit states.

Of all the Rydberg states identified in this study, it is the
pair of features at 56 312 and 56 965 cm\(^{-1}\) attributable to the
excited configuration [\(\Pi_u\)]4s\,\pi_u, and the pairs of states
derived from the respective configurations [\(\Pi_u\)]4p\,\pi_u
and [\(\Pi_u\)]4p\,\pi_u] that least conform to the Hund’s case (c)
labelling scheme. In each case the measured energy separation is
substantially greater than the 440 cm\(^{-1}\) spin–orbit splitting in
the ground state ion, implying a significant contribution from
the exchange energy. This is as is to be expected, since it is
in these lowest energy Rydberg states that the Rydberg
electron will show the greatest core penetration and thus that the
exchange interaction with the core should be greatest. We
can gain some estimate for the magnitude of \(K\) in each of
these cases if we assume the simple two state interaction
model implied by Fig. 8, i.e., if we assume that the only
interaction is between states belonging to the same [\(\Pi_u\)]n\(\lambda\)

\[\text{Three photon resonances}\]

The 61 000–67 000 cm\(^{-1}\) region shown in Fig. 1 has
been the subject of many previous experimental investiga-
tions, involving both one photon absorption spectroscopy\(^{1,5,8,13,14}\) and multiphoton excitation
methods,\(^{37–40}\) but the assignment of the observed resonances
has remained a matter of some controversy. Guided by sym-
metry and quantum defect considerations, by our analyses of the
accompanying REMPI-PE spectra, and in accord with the
conclusions of several of the earlier one photon absorption
\(^{8,13}\) and the more recent REMPI studies,\(^{39,40}\) we
assign the three photon resonances centered at 62 100 and
62 780 cm\(^{-1}\) as the electronic origins of the first (\(n=4\))
members of the [3/2]np\,\pi_u,\(\left(\Pi_u\right)\)–\(\tilde{X}1\Sigma_g^+\) and
[1/2]np\,\pi_u,\(\left(\Pi_u\right)\)–\(\tilde{X}1\Sigma_g^+\) series. Both of these features
were also evident in the earlier 3+1 REMPI spectrum
reported by Li et al.;\(^{37}\) these workers adopted the same inter-
pretation for the higher energy feature, but offered no assign-
ment for the 62 100 cm\(^{-1}\) resonance. Magnetic circular
dichroism measurements\(^{58}\) also support the assignment of the
62 780 cm\(^{-1}\) feature in terms of a perpendicular transition,
but this group chose to assign the 62 100 cm\(^{-1}\) transition as a hot band—a suggestion which the present
REMPI-PE spectra unambiguously refute. The quantum def-
ects for these two states (\(\delta=1.61\) and 1.60, respectively,
assuming that \(n=4\)) are entirely consistent with their assign-
ment in terms of excitation to a \(p\) Rydberg orbital.

A more serious point of contention in this region of the
3+1 REMPI spectrum concerns the assignment of the two
strong resonances centered at 63 644 and 64 209 cm\(^{-1}\). Having
previously identified two photon resonances [by two color (1+1)\(^+\) 1 REMPI spectroscopy\(^{58}\)] which they as-
signed in terms of the [3/2]3\(\delta_\pi,\left(\Delta_u\right)\)–\(\tilde{X}1\Sigma_g^+\) and
[1/2]3\(\delta_\pi,\left(\Delta_u\right)\)–\(\tilde{X}1\Sigma_g^+\) Rydberg excitations in this
energy region, Li et al.\(^{37,38}\) chose to assign these features in
terms of transitions to excited levels of these gerade elec-
tronic states carrying one quantum of the \(\pi_u\) bending vibra-
tion, \(v_2\). REMPI-PES offers a means of testing these assign-
ments and, in this particular case, as Figs. 5(b) and 5(c)

\[\text{FIG. 8. Diagram showing the correlations between states arising from a}\]

\[\text{\(\pi\) configuration when using the alternative \(\Lambda, S\) [Russell–Saunders, or}\]

\[\text{case (a)] and \(\Pi, \omega\) [case (c)] coupling schemes. The level labels 1\(^{1}\), and 1\(^{1}\)}

\[\text{denote \(1\) and 1\(^{1}\) as discussed in Ref. 57.}\]
The REMPI spectrum of CS$_2$ with the aid of REMPI-PES can be shown in Fig. 9 and the band contours of the corresponding dissociation becomes increasingly efficient as we ascend in components of the ground state ion. The Rydberg complex and with a common $\Omega$. Such a model implies values of $K$ in the range 240–260 cm$^{-1}$.

As Table II shows, most of the other significant features we identify in the 61 000–67 000 cm$^{-1}$ region of the 3+1 REMPI spectrum of CS$_2$ with the aid of REMPI-PES can be plausibly assigned in terms of transitions involving vibrationally excited states built upon the various recognized $^3\Pi_g^\prime$ origins. Moving to higher energies (Fig. 2), we identify strong 3+1 MPI resonances attributable to most of the corresponding spin–orbit split $^3\Pi_g$ origins (see Table II). We note that these assignments represent a substantial refinement over those derived from previous analysis of the room temperature one photon vuv absorption spectrum. Our inability to observe any higher $(n>5)$ members of these Rydberg series in the 3+1 REMPI spectrum suggests that, as in CO$_2$, pre-dissociation becomes increasingly efficient as we ascend in $n$ (and in energy).

Above 74 000 cm$^{-1}$ the 3+1 REMPI spectrum of CS$_2$ shows a dense progression of sharp bands which can be arranged into clumps which fit into two well defined series, split by ca. 440 cm$^{-1}$, converging to the two spin–orbit components of the ground state ion (see Table III). The accompanying REMPI-PE spectra show these to be origin transitions, while the fact that these series members are not apparent in the one photon absorption spectrum and in energy.

Above 74 000 cm$^{-1}$ the 3+1 REMPI spectrum of CS$_2$ shows a dense progression of sharp bands which can be arranged into clumps which fit into two well defined series, split by ca. 440 cm$^{-1}$, converging to the two spin–orbit components of the ground state ion (see Table III). The accompanying REMPI-PE spectra show these to be origin transitions, while the fact that these series members are not apparent in the one photon absorption spectrum and in energy.

Figure 3 illustrated the fact that the lower energy part (wavelengths larger than 290 nm) of the mass resolved 2+1 REMPI spectrum of CS$_2$ is greatly complicated by the presence of overlapping features due to valence excitations resonant at the one photon energy (i.e., 1+2 REMPI transitions). This near uv region of the one photon absorption spectrum of CS$_2$ has been the subject of fairly detailed investigations in the past and the positions of many of the more prominent band heads are well documented. REMPI spectroscopy, when allied with the facility to measure photoelectron kinetic energies, provides a particularly straightforward and convenient means of distinguishing the 1+2 and 2+1 resonances in this spectral region. This selectivity arises as a result of the differing equilibrium geometries of the states resonant at the one and two photon energies. The two photon resonances involve linear Rydberg states with little vibrational excitation; their subsequent one photon ionization tends to be vibrationally adiabatic (recall Figs. 5–7) and the kinetic energies of the resulting photoelectrons generally approach the limiting values allowed by energy conservation. In contrast, the one photon resonances involve bent valence states with equilibrium geometries very different from that of the (linear) ground state ion. Thus the Franck–Condon factors associated with the subsequent two photon ionization step will favor population of a wide spread of (excited) vibrational levels of the ion, and the accompany photoelectrons will have correspondingly less kinetic energy.

This selectivity is illustrated in Fig. 10: The upper spectrum, an expanded portion of the spectrum shown in Fig. 3 taken using mass selective detection of the parent ions ($m/z$ 76), contains both one and two photon resonances while the lower spectrum, obtained by monitoring just those photoelectrons with kinetic energies greater than ca. 0.35 eV, shows only the two photon resonances reported previously by Couris et al. The different spectral widths of these features in the two spectra are largely attributable to the broader rotational envelope associated with the near room temperature sample used in the REMPI-PES study. Analyses of the photoelectron spectra accompanying these two resonances (Fig. 7), and the deduced quantum defects of these two bands (δ~1.9, assuming $n=4$), are both consistent with previous assignments that these two features correspond to the $^3\Pi_g 4s\sigma_g^\prime X\Sigma_g^+$ and $^3\Pi_g 4s\sigma_g^\prime X\Sigma_g^+$ Rydberg origins, respectively. Several features which can be plausibly assigned as higher members of these two series are clearly identifiable in Fig. 3, though the $n=5$ members (centered at ca. 69 414 and 69 847 cm$^{-1}$) appear surprisingly broad (perhaps on account of a reduced lifetime as a consequence of predissociation). Additionally, the $n=7$ member of the latter series appears anomalously weak and, as Fig. 11 shows, was in fact only identified in the spectrum recorded using photoelectron (rather than ion) detection; these various origins are listed in Table IV.

Finally we comment on the $d$ Rydberg origin identified at 63 323 cm$^{-1}$ in the previous two color (1+1')+1 REMPI study. This region of the 2+1 REMPI spectrum of CS$_2$ is
heavily congested by the overlapping one photon resonances associated with vibronic levels of the bent valence states, to the extent that we were unable to identify this feature in the present work, even with the potential discrimination afforded by monitoring just a kinetic energy selected portion of the total photoelectron yield. This we attribute to a combination of spectral congestion and the weakness of the two photon REMPI transition via this \( 2 \Pi_g \) \( → \chi^1 \Sigma_g^+ \) Rydberg origin—presumably, as with the \( 2 \Pi_g \) \( np \) Rydberg states, because of the photoelectron kinetic energy chosen, only the latter contribute in spectrum (b). The vibronic assignments indicated in (a) are taken from Ref. 2.

As commented earlier, REMPI spectra obtained by monitoring the \( m/z \) 12, 32, and 44 mass channels each show structure that is clearly different from that associated with formation of the parent ion, thus indicating the formation of (and subsequent REMPI of) neutral C, S, and CS fragments in the present experiments. Figure 12 shows one of the more prominent features appearing in the \( m/z \) 44 mass channel—a blue degraded band which, by comparison with the earlier work of Ono and Hardwick, we attribute to a \( 1 \Pi_g \) \( → \chi^3 \Sigma_g^+ \) transition. Energetic considerations sug-

![Diagram](image1)

**FIG. 10.** Detail of part of the overall three photon ionization spectrum of CS\(_2\) obtained by monitoring (a) the yield of parent ions, and (b) the yield of photoelectrons with kinetic energies greater than ca. 0.35 eV, as a function of excitation wavelength. As discussed in the text, the former spectrum (a) contains a superposition of one and two photon resonances associated with excitations to bent valence states and linear Rydberg states, respectively, while, because of the photoelectron kinetic energy chosen, only the latter contribute in spectrum (b). The vibronic assignments indicated in (a) are taken from Ref. 2.

![Diagram](image2)

**FIG. 11.** Detail of the 74 500–78 000 cm\(^{-1}\) region of the 2+1 REMPI spectrum of a room temperature sample of CS\(_2\) obtained by monitoring the total photoelectron current as a function of excitation wavelength which serves to highlight the anomalous weakness of the \( [1/2]s \sigma^+_g \), \( (\Pi_g) → \chi^1 \Sigma_g^+ \) resonance.

<table>
<thead>
<tr>
<th>( n^* ) (cm(^{-1}))</th>
<th>Ion core</th>
<th>( n^* )</th>
<th>3+1/2+1</th>
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<tbody>
<tr>
<td>68 946</td>
<td>[3/2]</td>
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<tr>
<td>69 246</td>
<td>[1/2]</td>
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<td>76 520</td>
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</tbody>
</table>

**TABLE V.** Wave numbers, ion core symmetry, and effective quantum numbers (\( n^* \)) for unassigned two and three photon resonances. REMPI-PE spectroscopy indicates that all these resonance enhancements involve electronic origins save for the 74 128 cm\(^{-1}\) feature which was too weak to record a meaningful photoelectron spectrum.
suggest that these CS(a 3Π) fragments arise as a result of the following spin-allowed two photon dissociation:

\[
\text{CS}_2 \rightarrow \text{CS}(a \, 3\Pi) + \text{S}(3P_J)
\]

the thermochemical threshold for which is ca. 63 500 cm\(^{-1}\).\(^9\) Black et al.\(^{18}\) have reported the excitation spectrum for forming electronically excited CS(a 3Π) fragments in the one photon dissociation of CS\(_2\) and shown that the quantum yield for process (3) rises sharply as soon as the energetic threshold (λ ~ 158 nm) is exceeded. The present observations of structured resonances in the region expected for the \(\Delta v = -2, -1, 0\) transitions of the CS(\(^1\Sigma^+ \rightarrow a \, 3\Pi\)) transition (centered around excitation wavelengths of 300, and 291, and 282 nm, respectively) indicates the following: First, it suggests that the same dissociation channel can be reached via both one and two photon absorptions. Second, it provides some clues about the energy disposal in the fragments and thence about the photodissociation dynamics. As Fig. 12 shows, only the long wavelength part of this band (notably the \(P_{13}\) branch, and the \(Q_{13}, P_{23}\) band head)\(^{59}\) has proved amenable to spectral simulation: At shorter wavelengths the congestion from overlapping branches, the probable involvement of the (1–2) band, and the indeterminate and, in all likelihood, wavelength dependent rotational state population distribution within the nascent CS(a) photofragments makes a complete band contour simulation impossible. Nonetheless, the breadth of the 1+1 REMPI bands implies that the CS(a 3Π) fragments are formed rotationally excited (our crude assignment assumes a rotational temperature of 2000 K), while our observation of the (0–2) band at an excitation wavelength where CS(a 3Π)→ hole fragments are only just energetically allowed (by a two photon dissociation of CS\(_2\)) suggests that the dissociation dynamics also favor energy disposal into product vibration.

REMPI signals attributable to ground state C atoms arising in the multiphoton dissociation and/or ionization of CS\(_2\) were observed at excitation wavelengths ca. 287 and 280 nm (2+1 REMPI) and ca. 395 nm (3+1 REMPI). As Fig. 13 shows, the former exhibit the full multiplet structure expected\(^{46,61}\) of the \(3D_J \rightarrow 3P_J\) and \(3P_J \rightarrow 3P_J\) two photon resonances associated with the electron promotion \(2p^1\,3p^1 \rightarrow 2p^2\). Further discussion of these various atomic resonances and observed S atomic resonances is probably unwarranted given our lack of knowledge about the various C and S atom production mechanisms.

**CONCLUSIONS**

This study of the Rydberg state spectroscopy of the CS\(_2\) molecule in the energy range 56 000–81 000 cm\(^{-1}\) provides further illustration of the wealth of detailed information that can be gleaned from carefully studies involving the REMPI technique, especially when combined with parallel measurements of the kinetic energies of the resulting photoelectrons. The present study affords

(i) the most complete explanation yet available for the pattern of tangled spin–orbit split vibronic structure associ-
ated with the $^3\Pi_u$ and $^1\Pi_u$ states derived from the configuration $[\Pi_g^s]4p\sigma_u$ and the $^3\Delta_u$, $^1\Delta_u$, and $^1\Sigma_u^+$ states resulting from the configuration $[\Pi_g^s]4p\pi_u$, and allows estimation of an approximate wave number for the origin of the hitherto unidentified $^3\Sigma_u^+$ state derived from this same $[\Pi_g^s]4p\pi_u$ configuration;

(ii) determination of the origins of the next ($n = 5$) members of four of these $[\Pi_g^s]np$ Rydberg series;

(iii) identification of extensive series based on the Rydberg configurations $[\Pi_g^s]n\sigma_u$ and $[\Pi_g^s]n\pi_u$ with, in both cases, $n \approx 10$.

We also identify MPI resonances attributable to CS($a^3\Pi$) fragments, to ground state C atoms, and to S atoms in both their ground ($^2P$) and excited ($^2S$) electronic states. Analysis of the former resonances indicates that the CS($a^3\Pi$) fragments resulting from two photon dissociation of CS$_2$ at excitation wavelengths ca. 300 nm are formed with substantial rovibrational excitation.

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