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Resonance-enhanced Multiphoton Ionisation Spectroscopy of Thiirane

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We present a new and more extensive interpretation of the vertical electronic spectrum of the thiirane molecule based on (i) analysis of observed two- and three-photon resonance enhancements in the wavelength-resolved multiphoton ionisation spectrum of jet-cooled thiirane and (ii) measurements of the kinetic energies of the photoelectrons accompanying the multiphoton ionisation process. Six Rydberg series are identified, including the four series identified in previous one-photon vacuum ultraviolet absorption studies of this molecule. Series assignments are offered based on the measured quantum defects, their relative two- and three-photon transition strengths and the dependence (if any) of the two-photon transition intensities upon changing from linearly to circularly polarised photoexcitation. Our analysis suggests that, as in H₂S, many of the Rydberg orbitals have hybrid / character; it also points to the need for some revision of all previous interpretations of the electronic spectrum of the thiirane molecule.

Multiphoton excitation methods are increasingly finding use as a means of providing new spectroscopic and dynamical information about the excited electronic states of small and medium-sized molecular species.¹ This paper demonstrates the way in which, through use of a range of multiphoton spectroscopy methods, it has been possible to obtain the first comprehensive and internally consistent interpretation of the vertical electronic spectrum of the three-membered heterocycle thiirane (ethylene sulfide, H₂C⁻SC⁻H₂). Several experimental²⁻⁵ and theoretical⁶ studies of the vertical electronic spectrum of thiirane have been reported previously; most interpretations to date have been based on comparison with the prototypical dihydride, hydrogen sulfide.⁷ Such comparisons have been justified by the fact that, in both molecules, the highest occupied molecular orbital in the respective ground electronic states is largely non-bonding, being well approximated as the 3p_x orbital of atomic sulfur. The one-photon absorption spectra of both molecules exhibit a region of continuous absorption in the near UV followed, at shorter wavelengths, by numerous sharper vibronic features which have been assigned in terms of Rydberg series converging to the ground-state ion. Extrapolation of these various series has yielded values for the respective first ionisation potentials of H₂S^{8,9} and thiirane⁵ ($84\,428 \pm 10$ and $73\,090 \pm 60$ cm⁻¹, respectively) in good accord with those determined both by conventional HeI photoelectron spectroscopy¹⁰⁻¹² and, more recently in the case of H₂S, by two-photon non-resonant zero-kinetic-energy (ZEKE) photoelectron spectroscopy.¹³

Unambiguous assignment of the structured Rydberg features in the electronic absorption spectrum of thiirane is complicated by the fact that spectral congestion, almost certainly compounded by predissociation broadening, precludes observation of any rotational fine structure. Previous experimental analyses²⁻⁵ of the Rydberg structure exhibited by this molecule have thus been based largely on determination of the quantum defects, δ , of the various features, and analogy with the then-existing interpretations of the vertical electronic spectrum of H₂S. The validity of the latter strategy must be

questioned, however, since both recent two-photon resonant multiphoton ionisation (MPI) spectroscopy experiments involving the H₂S molecule¹⁴ and recent *ab initio* calculations of the vertical electronic spectra of both H₂S¹⁵ and thiirane⁶ have indicated the need for some revision of the traditional assignments. In particular, the recent experimental¹⁴ and theoretical¹⁵ studies have served to highlight the 'atomic-like' nature of the Rydberg transitions in H₂S and the propensity for odd(even) changes in the *l* quantum number in electronic transitions brought about by the absorption of an odd(even) number of photons. Given these concerns, and the presumed parallels between H₂S and thiirane, it seemed worthwhile to record multiphoton excitation spectra of thiirane in order to try to gain further insight into the nature and energetic ordering of the excited electronic states in this molecule.

Here we report the results of a systematic study of the two- and three-photon resonance-enhanced multiphoton ionisation (REMPI) spectra of thiirane, and a small portion of the corresponding one-photon spectrum. The multiphoton spectra both show a wealth of resolved vibronic structure, much of which can be arranged into well defined Rydberg series converging to the ground-state ionisation limit. The interpretation of individual vibronic features appearing in these spectra has been greatly aided by concurrent measurements of the kinetic energies of the photoelectrons accompanying the MPI process, whilst series assignments have been guided by quantum defect considerations, by the relative intensities of the series members in the two- and three-photon excitation spectra and, in appropriate cases, by the observed change in the two-photon band intensities upon switching from linearly to circularly polarised photoexcitation.

Experimental

The results reported herein were obtained using two complementary apparatus. Mass-resolved MPI spectra of thiirane were recorded in Bristol by expanding the pure gas (Aldrich, 98%, backing pressure *ca.* 1 atm) through a pulsed nozzle into the source region of a home-built time-of-flight (TOF) mass spectrometer.^{14,16} Two-photon REMPI spectra at excitation wavelengths shorter than 335 nm were recorded using the frequency-doubled output of an Nd:YAG pumped dye

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laser (Spectron 803 plus SL4000 together with an Inrad 'autotracker' system employing a selection of KDP or β -barium borate doubling crystals). The longer wavelength portion of the two-photon excitation spectrum, and the corresponding three-photon REMPI spectrum, were recorded using an excimer pumped dye laser (Lambda Physik EMG 201 and FL 2002). In all cases the output radiation was focussed ($f = 200$ – 300 mm) into the source region of the TOF mass spectrometer so as to interrogate the gas pulse at its point of maximum flux. Under normal operating conditions both laser outputs were linearly polarised, with their electric vector aligned perpendicular to the TOF axis. When necessary, these outputs could be circularly polarised by insertion of an appropriately oriented Fresnel rhomb. Ions formed in the source region were subjected to two stages of acceleration before entering a field-free drift region and ultimate detection by a channel electron multiplier. TOF spectra were obtained by feeding the amplified output from this multiplier into a fast digital oscilloscope (LeCroy 9400, 125 MHz bandwidth) and thence, *via* an IEEE interface, to a 386 PC. MPI spectra associated with the formation of a particular ion mass were obtained by scanning the laser wavelength and collecting that fraction of the total ion signal that fell within the user-selected narrow time-window spanning the appropriate TOF. Wavelength calibration, in the visible, was achieved by simultaneously recording the optogalvanic spectrum of neon excited in a hollow cathode discharge.

REMPI photoelectron spectra (PES) were recorded in Amsterdam using a 'magnetic bottle' spectrometer the design

and operation of which have also been detailed previously.^{17,18} Briefly, light from an excimer pumped dye laser system (Lumonics HyperEx-460 and HyperDye-500), doubled in frequency if necessary using a frequency doubling unit (Lumonics Hypertrak-1000), is focussed ($f = 25$ mm) into the ionisation region of the electron spectrometer where it intercepts an effusive beam of pure thiirane vapour. Approximately 50% of the photoelectrons resulting from each laser pulse are extracted into the spectrometer and their kinetic energies determined *via* their measured times of arrival at a pair of microchannel plates situated at the end of the 500 mm flight tube. The signal from the microchannel plates is pre-amplified and passed to a transient digitiser, which is interfaced to a PC to enable further data manipulation and analysis. A PE spectrum is constructed by increasing the retarding voltage on a grid in the flight tube in a stepwise fashion, and transforming only the high-resolution part of the TOF spectrum. In this way it was possible to achieve 15 meV (FWHM) resolution at all kinetic energies in the present experiments. The measured electron kinetic energies were placed on an absolute scale by doping the thiirane sample with xenon and measuring, simultaneously, the kinetic energies of electrons resulting from well documented REMPI transitions terminating on the two spin-orbit states of the Xe^+ ion.

Results and Discussion

Fig. 1 displays a composite three-photon REMPI spectrum of thiirane (*i.e.* involving resonances in the wavenumber

Fig. 1 3 + 1 MPI spectrum of thiirane over the wavelength range 540–417 nm recorded using linearly polarised light and monitoring only those ions with times-of-flight appropriate to m/z 45 and/or 60. The displayed spectrum is a composite, obtained by splicing together spectra recorded using five different dyes. As discussed in the text, we have not taken any particular steps to ensure correct normalisation of the relative intensities of features appearing within the tuning range of any one dye, or between one dye tuning curve and the next. Arrows indicate the wavelengths at which we switched from one dye to another. Members of the Rydberg series that appear clearly as three-photon resonances are indicated *via* the combs superimposed over the spectrum. The indicated principal quantum numbers, n , are consistent with the dominant $n'l' \leftarrow 3b_1$ assignments offered in Table 1. $E_1 = 73\,090\text{ cm}^{-1}$

Fig. 2 2 + 1 MPI spectrum of thiirane over the wavelength range 390–278 nm recorded using linearly polarised light and monitoring only those ions with times-of-flight appropriate to m/z 59 and/or 60. As in Fig. 1 the displayed spectrum is a composite, and the same comments apply. Members of the Rydberg series that appear clearly as two-photon resonances are indicated *via* the combs superimposed over the spectrum.

range 55 300–72 000 cm^{-1}) recorded using linearly polarised laser radiation in the wavelength range 540–417 nm. Fig. 2 shows the corresponding linearly polarised two-photon REMPI spectrum, recorded using excitation wavelengths in the range 390–278 nm (corresponding two-photon wavenumber range 51 500–72 000 cm^{-1}). Clearly, the two show significant differences. At this point, we comment that we are here interested primarily in the peak positions and caution against reading too much into the relative intensities of the various peaks in these spectra. As in any REMPI spectrum, these spectra will tend to be dominated by transitions involving the less predissociated excited states; however, simply by increasing the laser intensities it is possible to enhance the relative showing of transitions involving more short-lived excited states.^{1,19} The present spectra were recorded using a number of different dyes; we have not taken any particular care about normalising the laser power either between dyes, or within the tuning range of any one dye. Ion fragmentation is a further factor affecting the relative peak intensities. The spectra shown in Fig. 1 and 2 were obtained by monitoring the wavelength dependence of one or more specific features in the TOF spectrum, *e.g.* the parent ion peak. However, as Fig. 3 shows, the relative showing of the various m/z peaks observed at any one wavelength varies with the incident pulse energy. The relative peak intensities also vary with excitation wavelength, with fragmentation becoming increasingly prevalent as we scan to shorter wavelengths. Checks were made to confirm that, for any given set of experimental conditions (*i.e.* laser polarisation, intensity *etc.*), the excitation spectra for all of the major molecular ion peaks exhibit the same pattern of band positions though, inevitably, there are some variations in relative peak intensities. We reserve discussion of these fragmentation patterns until later in this section.

Fig. 3 Ion TOF spectra obtained following REMPI at 329.2 nm using laser pulse energies of (a) 3.5 and (b) 1.5 mJ. These show clearly the increased fragmentation that results when using higher incident light intensities.

REMPI-PES

In common with previous workers, we shall attempt to assign the observed features as members of Rydberg series converging to the first ionisation potential. Tokue *et al.*⁵ derived a value $E_i = 73\,090 \pm 60 \text{ cm}^{-1}$ by extrapolating one of the more prominent series in the one-photon absorption spectrum of thiirane. We determine an identical value for E_i from measurements of the photoelectron kinetic energies arising in the REMPI of thiirane. Fig. 4 shows three illustrative REMPI-PES. The first [Fig. 4(a)], obtained following excitation of thiirane at 497.1 nm, is dominated by a single peak with a maximum at 0.912 eV (7360 cm^{-1}). This spectrum can be understood most simply by assuming that the electrons arise as a result of a three-photon resonance-enhanced, four-photon ionisation process. All of the measured REMPI-PES are consistent with ionisation occurring *via* an $n+1$ process. In this particular case the spectral simplicity suggests that the final one-photon ionisation from the resonance-enhancing Rydberg level involves a $\Delta v = 0$ transition. Furthermore, our inability to discern any faster electrons in this PES encourages the assumption that the parent ion is formed in its vibrationless level and thus that the resonance enhancement involves an electronic origin transition. Given this assumption, the measured photoelectron kinetic energy implies a

Fig. 4 MPI-PES taken following excitation at: (a) 497.1 nm ($60\,358 \text{ cm}^{-1}$) where we excite a three-photon resonance involving the origin level of the state we identify as the first member of Series V; (b) 328.9 nm ($60\,805 \text{ cm}^{-1}$), for which the process is resonance enhanced at the two-photon energy by the origin level of the first member of our Series II; (c) 323.3 nm ($61\,845 \text{ cm}^{-1}$). The kinetic energy of the dominant peak in this spectrum is consistent with the partner ion carrying *ca.* 1050 cm^{-1} of internal energy. Thus we deduce that the ion and, *via* Franck-Condon arguments, the resonance-enhancing level at the two-photon energy both involve one quantum of the ν_4 vibration.

value for the first adiabatic ionisation potential of thiirane identical to that reported previously by Tokue *et al.*⁵

The photoelectron spectra shown in Fig. 4(b) and (c), obtained following excitation at 328.9 nm and 323.3 nm, respectively, provide further examples of multiphoton excitations in which the final ionisation step shows a strong propensity for being Franck-Condon diagonal. In both cases the resonance enhancement occurs at the two-photon level, and the electron kinetic energies are consistent with ion formation involving absorption of a total of three photons. In the former PES, the measured photoelectron kinetic energy of the major peak [2.246 eV ($18\,120 \text{ cm}^{-1}$)] indicates that the parent ion is formed predominantly in its ground vibrational state; this, in turn, suggests that the resonance enhancement involves a vibrationless Rydberg level. However, in the latter PES [Fig. 4(c)], the peak associated with formation of the vibrationless ion [at a kinetic energy of 2.440 eV ($19\,680 \text{ cm}^{-1}$)] is weak. The dominant peak occurs at lower kinetic energy, indicating that most of the ions are formed with *ca.* 130 meV (1050 cm^{-1}) of internal energy. This separation is reminiscent of the energy spacings between the short progression of features observed in the conventional one-photon PES of thiirane^{10,11} and, as in these earlier studies, we attribute it to excitation of the ν_4 mode (a totally symmetric mode involving concerted CH_2 wagging and ring breathing motions) of the parent ion. Franck-Condon considerations then point to the likelihood that the excited vibronic level of the neutral providing the resonance enhancement at the two-photon energy carries one quantum of ν_4 . This conclusion gains added weight once we recognise that the two-photon resonances that give rise to the two PES shown in Fig. 4(b) and (c) are themselves separated by essentially the same interval, 1040 cm^{-1} .

The availability of PES such as these, and the insight they provide concerning the vibronic character of the resonance-enhancing level, proved to be absolutely crucial to the analysis of the REMPI spectra shown in Fig. 1 and 2. As a final example of the way in which such PES can aid in spectral assignment, consider the triplet of strong three-photon resonances observed at excitation wavelengths *ca.* 500 nm (Fig. 1). We have already seen from the PES shown in Fig. 4(a) that the central feature ($\lambda_{\text{exc}} = 497.1 \text{ nm}$) can be assigned to an origin transition. What should we make of the two neighbouring features, which are both obvious as three-photon resonances at $\lambda_{\text{exc}} = 501.0 \text{ nm}$ and 495.8 nm but barely discernible as two-photon resonances? Neither obviously fits as part of a Rydberg series, yet the apparent strength of the three-photon resonances might seem to mitigate against their assignment in terms of transitions involving vibrationally excited levels of a Rydberg state derived from excitation of what is, essentially, a non-bonding electron. However, the associated REMPI-PES [Fig. 5(a) and 5(b)] show that this, indeed, is how they should be viewed.

Consider first the higher-frequency peak observed at an excitation wavelength of 495.8 nm (corresponding three-photon wavenumber $3\bar{\nu} = 60\,504 \text{ cm}^{-1}$): The $3+1$ REMPI-PES [Fig. 5(b)] is dominated by two features, one corresponding to the formation of vibrationless ions, the other to ions with some 420 meV (3150 cm^{-1}) of internal energy. We note that this three-photon resonance occurs similarly shifted (by *ca.* 3020 cm^{-1}) from a demonstrable origin transition at $57\,481 \text{ cm}^{-1}$. Built upon the faster of the two strong PES features is a progression of peaks separated by *ca.* 141 meV (1120 cm^{-1}), each of which appears with a satellite shifted some 67 meV (540 cm^{-1}) to higher energy. Guided by the earlier *ab initio* calculations,⁵ we associated these intervals with excitation of, respectively, the ν_3 and ν_5 modes of the ion. The first of these two totally symmetric vibrations

Fig. 5 MPI-PES taken following excitation at (a) 501.0 nm (59 883 cm^{-1}), (b) 495.8 nm (60 504 cm^{-1}) and (c) 488.9 nm (61 362 cm^{-1}). The REMPI-PES reveal that, in each case, the resonance-enhancing level at the three-photon energy should be viewed as a vibrationally excited level of the Series IV member whose origin appears at 57 481 cm^{-1} .

involves a concerted C—C stretching and CH_2 wagging motion, whilst the latter, low-frequency, mode is associated with motion of the S atom along the C_2 axis perpendicular to the C—C bond. The simplest interpretation of these observations is that the 60 504 cm^{-1} resonance is associated with a three-photon transition to a level which, in a zero-order description, involves ca. 3020 cm^{-1} of vibrational energy (at least part of which is concentrated in the ν_3 and ν_5 modes). Because of its accidental near-degeneracy, this zero-order state ψ_v mixes with, and gains transition intensity from, the Rydberg origin state (zero-order wavefunction ψ_R) observed as a particularly strong three-photon resonance at $3\bar{\nu} = 60\,358\text{ cm}^{-1}$. A similar explanation most likely accounts for the lower-frequency resonance observed at $3\bar{\nu} = 59\,883\text{ cm}^{-1}$, ca. 2400 cm^{-1} above the 57 481 cm^{-1} Rydberg origin. The REMPI-PES in this case [Fig. 5(a)] also shows two dominant peaks; again, the faster feature is attributable to the formation of vibrationless ions whilst the slower electrons must rise in association with ions with ca. 337 meV (2720 cm^{-1}) of internal energy. Once again, the REMPI-PES also displays a progression in the 141 meV (1120 cm^{-1}) mode of the ion and peaks associated with excitation of one quantum of the 67 meV (540 cm^{-1}) vibration. The pattern of vibronically induced resonances is repeated ca. 1050 cm^{-1} to higher energy in the 3 + 1 REMPI spectrum; these we attribute to the same pattern of three interacting states, with the transition strength now provided by the three-photon reson-

ance involving the 4^1 level of the Rydberg state whose origin appears at 60 358 cm^{-1} . As expected, the REMPI-PES associated with each of these three resonances display a pattern of features very similar to that shown by their respective counterparts at lower energy, each shifted in energy by an amount corresponding to one quantum of ν_4 in the ion, and each showing one (or two) higher-kinetic-energy peaks associated with ion formation in its ground vibrational state, and with one quantum in the low-frequency ν_5 mode. Fig. 5(c) provides one illustrative example. In concluding this section, we should comment that since the actual eigenstates associated with each of these three interacting levels have a wavefunction of the general form $(a\psi_R + b\psi_v)$ then the REMPI-PES obtained following excitation *via* what, in a zero-order description, we would regard as the Rydberg origin level should, in fact, be contaminated by slower electrons associated with vertical one-photon ionisation of the ψ_v component of the wavefunction. Comparison of the REMPI-PES displayed in Fig. 4(a) and (b) show that, at least qualitatively, this is the case.

Assigning the Multiphoton Resonances

Armed with this insight into the vibronic character of the various resonance-enhancing levels we are now in a position to offer a global assignment of the excited electronic states of the thirane molecule. Band maxima ($\bar{\nu}$) measured in the present work are listed in Table 1. In the case of proposed Rydberg origins we also list the associated effective quantum numbers, n^* , calculated using the relationship

$$\bar{\nu} = E_i - R/(n^*)^2 \quad (1)$$

where $E_i = 73\,090\text{ cm}^{-1}$, R is the Rydberg constant (109 737 cm^{-1}) and $n^* = (n - \delta)$, with n being the principal quantum number and δ the quantum defect. For completeness, we also list the major peaks identified in the one-photon absorption studies of Basco and Morse³ and Tokue *et al.*⁵

Before embarking on a detailed discussion of these results it is instructive to consider the range of excited states we might expect. Ground-state thirane has C_{2v} symmetry. Adopting the convention that z corresponds to the C_2 axis and that the heavy atom ring lies in the yz plane, then the ground-state electronic configuration may be written

$$\dots (2b_1)^2 (7a_1)^2 (1a_2)^2 (8a_1)^2 (4b_2)^2 (3b_1)^2; \quad \bar{X}^1 A_1 \quad (2)$$

in which the highest occupied $3b_1$ orbital is largely comprised of the non-bonding sulfur $3p_x$ orbital, directed perpendicular to the plane containing the ring of heavy atoms.⁵ Promoting one $3b_1$ electron to higher nl Rydberg orbitals can be expected to give rise to one 's' ($l = 0$) series involving states of 1B_1 electronic symmetry and $n \geq 4$, three 'p' series (of 1B_1 , 1A_1 and 1A_2 symmetries, respectively, all with $n \geq 4$), five 'd' series (two of 1B_1 symmetry together with one each of 1A_1 , 1A_2 and 1B_2 symmetry, all with $n \geq 3$), seven 'f' series (two each transforming as 1A_1 , 1A_2 and 1B_1 , the other of 1B_2 symmetry, all with $n \geq 4$) *etc.* The quotation marks are included as a reminder that configuration mixing may render l an approximate label, whilst not invalidating the overall state count. Analogy with atomic sulfur and with H_2S suggests that 'pure' l series will exhibit quantum defects ca. 2.0 (s series), ca. 1.6 (p series) and ca. 0 (for d, f and higher l functions).^{7,9,14} Such expectations led Tokue *et al.*⁵ to propose the identification of one s ($\delta = 1.91$), one p ($\delta = 1.66$) and two d Rydberg series ($\delta = 0.35$ and 0.07 , respectively) in their one-photon absorption spectrum of thirane. Further, given that the second (adiabatic) ionisation potential of thirane (associated with removal of a $4b_2$ electron) lies at ca. 11.35 eV,^{11,12} it is unlikely that any features associated with

Table 1 Wavenumbers, effective quantum numbers (n^*) and proposed assignments of the thiirane resonances observed in the present multi-photon study. The l function we presume to be dominant in each of the Series I–VI is indicated (between quotation marks).

$\bar{\nu}/\text{cm}^{-1}$	n^*	vibronic assignment	one-photon VUV ^a	$\bar{\nu}/\text{cm}^{-1}$	n^*	vibronic assignment	one-photon VUV ^a
Series I ($n's'a_1 \leftarrow 3b_1$)				Series II ($n'p'a_1 \leftarrow 3b_1$)			
62 294	(2.06) 3.19		47 137	47 660	2.08		
63 345		4_0^1		60 805	2.99		
64 396		4_0^2		61 587		11_0^1	
66 898	4.21			61 845		4_0^1	
69 065	5.22			62 627		$4_0^1 11_0^1$	
				66 356	4.04		
				67 409		4_0^1	
				68 777	5.04		
				70 010	5.97		
				70 826	6.96		
				71 358	7.95		
				71 730	8.98		
				71 985	9.96		
Series III ($n'p'b_1 \leftarrow 3b_1$)				Series IV ($n'd'a_1 \leftarrow 3b_1$)			
51 986	2.28		52 029 (52 010)	57 481	2.65		57 508 (57 490)
52 510		5_0^1		58 200		11_0^1	
53 015		4_0^1	(53 087)	58 540		4_0^1	(58 535)
	(3.31)		63 119	59 884		(+ 2403 cm^{-1})	
67 235	4.33		67 308	60 504		(+ 3023 cm^{-1})	
69 202	5.31		69 286	64 789	3.64		64 821 (64 771)
70 360	6.34		70 428 (70 505)	68 080	4.68		67 939 (68 032)
				69 593	5.60		69 604 (69 592)
				71 221	7.66		71 159 (71 308)
Series V ($n'd'b_1 \leftarrow 3b_1$)				Series VI ($n'd'b_1 \leftarrow 3b_1$)			
60 358	2.94		60 507	61 316	3.05		61 286
61 370		4_0^1		62 392		4_0^1	
62 400		4_0^2		66 506	4.08		66 520
65 986	3.93		66 011 (65 970)	67 556		4_0^1	
67 038		4_0^1		68 854	5.09		68 856
68 543	4.91		68 592 (68 535)	69 910		4_0^1	(69 913)
69 929	5.89		69 984 (69 913)	70 129	6.09		70 112
				70 899	7.08		
				71 409	8.07		

^a Ref. 5, value in parentheses, ref. 3.

Rydberg states belonging to series converging to this second limit should appear at energies below *ca.* 68 000 cm^{-1} in the vertical excitation spectrum.

We now turn to discuss the various Rydberg series in turn. The lowest-energy feature identified in the multiphoton spectra appears as a two-photon resonance at 51 986 cm^{-1} (Fig. 2). We did not search for any three-photon resonance associated with this excited state since, at the relevant excitation wavelengths (*ca.* 584 nm) ionisation would require absorption of a further two photons; interpretation of any spectrum so obtained would thus be complicated by possible resonance enhancements at the energy corresponding to four absorbed photons. This same feature appears strongly ($\epsilon_{\text{max}} \approx 6 \times 10^{-17} \text{ cm}^2$) in one-photon absorption;^{2–5} two weaker features at higher energy have been assigned in terms of transitions to excited vibronic levels involving, respectively, one and two quanta of ν_4 . Basco and Morse³ originally proposed that this feature be viewed as the first member of the $ns \leftarrow 3b_1$ series but, given its quantum defect ($\delta \approx 1.72$, assuming $n = 4$) and the fact that dichroism measurements⁴ are consistent with the excited state having A_1 symmetry, assignment in terms of electron promotion to the $4p_{b_1}$ Rydberg orbital seems more reasonable. Recent *ab initio* calculations⁶ support this conclusion, though the intense showing of this transition in one-photon absorption must cast doubt on the purity of the $l = 1$ description. Evidence for the predissociative nature of this excited state is provided by

photofragment translational spectroscopy experiments,²⁰ which show C–H bond fission to be the dominant primary decomposition route following photoexcitation at 193 nm. $S(^1D)$ atom elimination is a minor (*ca.* 10%) competing fragmentation pathway at this wavelength; measurements of a positive recoil anisotropy parameter ($\beta \approx +1$) for these S atom products provides further confirmation of the A_1 excited-state symmetry.^{20,21} A number of higher-frequency features exhibiting similar δ values are grouped together as 'Series III' in Table 1. These are clearly evident (though with diminishing intensity) in the one-photon spectra reported previously^{3,5} but none show particularly clearly in the REMPI spectra, perhaps indicative of a short excited-state lifetime.

The next feature apparent in the two-photon REMPI spectrum is a weak, diffuse maximum centred around 54 800 cm^{-1} . This band has no reported counterpart in the one-photon spectrum. Given its quantum defect ($\delta \approx 1.55$, assuming $n = 4$) and the recent *ab initio* results,⁶ it is tempting to speculate that this resonance may be associated with the one-photon dipole-forbidden $^1A_2 \leftarrow \tilde{X}^1A_1$ transition arising as a result of electron promotion to the $4p_{b_2}$ orbital. If correct, the diffuseness of the observed resonance would suggest a significant antibonding valence contribution to the excited b_2 orbital. We were unable to recognise any higher-energy features that could obviously be arranged into a series with this 54 800 cm^{-1} band as first member.

The feature centred at 57481 cm^{-1} , which we see both as a two- and a three-photon resonance, also shows strongly in one-photon absorption.²⁻⁵ Electric dichroism measurements are consistent with the excited state having 1B_1 symmetry, and assignment in terms of the electronic promotion $3da_1 \leftarrow 3b_1$ has been proposed.⁴ The quantum defect ($\delta \approx 0.35$, assuming $n = 3$) is uncharacteristically large for a pure $l = 2$ function; this, and the fact that the resonance shows in one-, two- and three-photon absorption, indicates that the excited a_1 orbital probably has hybrid l character. Similar p/d mixing has been invoked previously to account for the relative strengths of Rydberg transitions observed in the multiphoton spectrum of H_2S and D_2S .¹⁴ Higher members of this series (labelled Series IV in Table 1) show strongly in one-photon absorption²⁻⁵ and are clearly evident as three-photon resonances in Fig. 1. However, inspection of Fig. 2 reveals that the $n > 3$ members of Series IV do not appear as two-photon resonances, perhaps indicating that, for this series at least, the extent of l mixing decreases rapidly with increasing n . Returning to the first ($n = 3$) member, we have already seen from their associated REMPI-PES [e.g. Fig. 5(a) and (b)] that several of the resonances appearing immediately to higher energy in both the two- and three-photon excitation spectra can be associated with vibrationally excited levels of this Rydberg state. These resonances are also listed in Table 1.

Series V, which dominates the spectrum shown in Fig. 1, also contributes two-photon resonance enhancements (Fig. 2) and has been identified previously in one-photon absorption²⁻⁵, though the earliest analysis³ failed to associate the first (60358 cm^{-1}) feature with this series. Short (one-member) vibronic progressions, involving v_4 built on this first origin and on the next series member (at 65986 cm^{-1}) are clearly evident in Fig. 1; the $n = 6$ member of Series IV overlaps the expected position for the 4_0^1 transition associated with the third member. Both Basco and Morse³ and Tokue *et al.*⁵ assign this series in terms of the excitation $nd \leftarrow 3b_1$ which, given the observed quantum defect ($\delta \approx 0.06$, assuming that the 60358 cm^{-1} member has $n = 3$), seems reasonable. However, the recent *ab initio* study⁶ advocated the alternative plausible assignment, namely that Series V in Table 1 be associated with the promotions $ns \leftarrow 3b_1$. In this interpretation, the 60358 cm^{-1} feature would involve excitation to the $5s$ orbital; the implied quantum defect ($\delta \approx 2.06$) is also reasonable. The present multiphoton studies provide a means of distinguishing between these two alternative assignments since, as Fig. 6 shows, we find that the relative intensities of the two-photon resonances we associate with Series V members decrease when we use circularly polarised light to record the spectrum. This is a characteristic diagnostic for a two-photon transition linking two states of the same symmetry, since only for such totally symmetric transitions can the scalar $[T^0(A)]$ part of the two-photon transition moment (the component that is forbidden in circularly polarised excitation) have non-zero amplitude. Thus we conclude that the excited states involved in Series V have 1A_1 electronic symmetry, and that the populated Rydberg orbitals have b_1 symmetry. This, in turn, provides strong support for the original experimental assignment of Series V in terms of the orbital promotion $ndb_1 \leftarrow 3b_1$. The fact that these states also appear as two-photon resonances, however, suggests a degree of d/p mixing in the Rydberg orbitals.

Our assignment of the Series IV and V members as having, respectively, 1B_1 and 1A_1 electronic symmetry allows further speculation on the nature of the vibronic interaction linking the states responsible for the three strong resonances appearing ca. 60300 cm^{-1} in the $3 + 1$ REMPI spectrum (Fig. 1). The PES [Fig. 4(a), 5(a) and (b)] led to the conclusion that the interacting zero-order states comprised the Series V $n = 3$

Fig. 6 $2 + 1$ MPI spectrum of thiirane over the wavelength range 333–289 nm recorded using (a) linearly and (b) circularly polarised light and monitoring only those ions with times-of-flight appropriate to m/z 59 and 60. As in Fig. 2 the displayed spectrum is a composite obtained using more than one dye, and the same comments apply. Two-photon resonance enhancements brought about by vibronic levels of A_1 symmetry are highlighted by the combs superimposed over the spectrum.

origin level (of 1A_1 electronic symmetry) and two vibrationally excited levels of the $n = 3$ member of Series IV. Given that this latter state is deduced to have 1B_1 electronic symmetry, vibronic interaction requires that the 'vibration' (be it a fundamental or a combination mode) has the overall vibrational symmetry b_1 . The form of the associated REMPI-PES [Fig. 5(a) and (b)] points to activity in the v_3 and v_5 modes of the ion (both of which are totally symmetric modes). Energetic considerations, together with the requirement that the overall combination has b_1 vibrational symmetry, then suggest the combinations $3^15^111^1$ and $3^15^211^1$ as plausible assignments for the vibrational contributions to the zero-order states contributing to the 59883 and 60504 cm^{-1} resonances. Vibronic interaction with the near-resonant 1A_1 electronic origin accounts for the appearance of resonances involving the non-totally symmetric v_{11} mode.

The REMPI-PES studies allow us to identify three further origin transitions in the energy region associated with near-integer n^* values. Two appear in the present multiphoton study exclusively as two-photon resonances, the third only as a three-photon resonance enhancement. We shall discuss these, and their associated series, in order of increasing energy. The first, which for reasons that become apparent later we shall label Series II, makes its first contribution to our two-photon REMPI spectrum through the feature centred at 60805 cm^{-1} [see Fig. 2 and the associated REMPI-PES displayed in Fig. 4(b)]. Higher members of this series can be identified immediately to lower frequency of the more intense Series VI origins (see below). As Fig. 6 illus-

trates, the relative showing of our Series II origin transitions are enhanced upon changing to circularly polarised excitation. Their quantum defects ($\delta \approx 0$, if we were to assume that the $60\,805\text{ cm}^{-1}$ feature has $n = 3$) might suggest an assignment in terms of an $nd \leftarrow 3b_1$ orbital promotion, but such an analysis runs contrary to any expected propensities based on atomic selection rules. The interpretation that follows is based on unravelling the vibronic structure that appears on the high-frequency side of the $60\,805\text{ cm}^{-1}$ member. The REMPI-PES studies confirm that the two-photon resonance at $61\,845\text{ cm}^{-1}$ is its associated $4b_1$ vibronic transition. More revealingly, the REMPI-PES studies indicate that the two very sharp peaks at $61\,587$ and $62\,627\text{ cm}^{-1}$ are also due to vibrationally excited levels of the state whose origin appears at $60\,805\text{ cm}^{-1}$. The two very sharp peaks are separated by 1040 cm^{-1} (a typical wavenumber for the ν_4 vibration which we see to be active in many of the Rydberg absorptions of thiirane), but the energy gap between the first of these two features and its electronic origin is only 782 cm^{-1} . Such a separation matches none of the totally symmetric vibrational modes of ground-state thiirane²² or its cation;⁵ once again, we invoke the involvement of the $\nu_{11}(b_1)$ vibration (824 cm^{-1} in the ground state neutral²²) and assign the two sharp peaks as the 11_0^0 and $4_1^1 11_0^1$ vibronic bands, respectively. Given that these excited levels have A_1 vibronic symmetry (from the fact that these two-photon resonances 'disappear' when excited using circularly polarised light), it therefore follows that the state responsible for the $60\,805\text{ cm}^{-1}$ resonance has 1B_1 electronic symmetry. Once again, we invoke vibronic mixing, in this case with the accidentally near-resonant 0^0 (and 4^1) levels of the excited state of 1A_1 electronic symmetry that provides two-photon resonance enhancement at $61\,316\text{ cm}^{-1}$ (and $62\,392\text{ cm}^{-1}$), as the source of the two-photon transition strength to these particular vibronic levels.

We now return to the question of the electronic configuration from which this 1B_1 Rydberg state is derived. As we have seen, simple quantum defect considerations suggest assignment of these resonances in terms of the orbital promotion $3da_1 \leftarrow 3b_1$ or $5sa_1 \leftarrow 3b_1$, whereas the observed two-photon transition strength is only compatible with the anticipated Δl propensity rule if we invoke significant p character in the Rydberg orbital. The *ab initio* calculations of Carnell and Peyerimhoff⁶ lend some support to this latter proposal. These workers⁶ reported calculated term values for the three members of the '4p-complex' spanning an energy spread of some 6400 cm^{-1} , with the 1B_1 member lowest in energy (close, in fact, to the 1B_1 state derived from the $4sa_1 \leftarrow 3b_1$ excitation) and exhibiting a quantum defect, $\delta \approx 1.90$. Indeed, so confident are Carnell and Peyerimhoff⁶ of their theoretical result that they go so far as to offer a reassignment of the poorly resolved vibronic structure seen in the earlier near-UV absorption studies of thiirane.^{2,5} To test this conclusion further, we searched for ions and/or photoelectrons arising as a result of two-photon ionisation, resonance-enhanced at the one-photon energy by the predicted $^1B_1(4pa_1)$ Rydberg state. Fig. 7 displays the spectrum obtained by monitoring the yield of parent ions as a function of excitation wavelength over the range $212.8\text{--}208.0\text{ nm}$. Strikingly, we see clear evidence for a feature at $47\,660\text{ cm}^{-1}$, hitherto associated with transition to the 5^1 component of the $^1B_1(4sa_1)$ state, but not the corresponding origin band (which appears in one-photon absorption at *ca.* $47\,137\text{ cm}^{-1}$ with substantially greater intensity). This can be understood if the higher-energy feature has a longer lifetime (and thus a higher ionisation probability). Such would be unusual (though not without precedent²³) if the two excited levels were associated with the same electronic state, but would be readily believable if the two levels were actually associated

Fig. 7 $1 + 1$ MPI spectrum of thiirane over the wavelength range $212.8\text{--}208.0\text{ nm}$ recorded using linearly polarised light and monitoring those ions with times-of-flight appropriate to $m/z\ 60$.

with two different electronic states. Precise measurement of the kinetic energies of the photoelectrons resulting from $1 + 1$ MPI via the $47\,660\text{ cm}^{-1}$ feature proved challenging: the REMPI-PES is found to be dominated by a single peak whose energy is consistent with formation of ground-state ions. Franck-Condon considerations thus point to the $47\,660\text{ cm}^{-1}$ feature being another origin band, in accord with the theoretical conclusions of Carnell and Peyerimhoff.⁶ Guided by these calculations, we propose that this origin be associated with the electronic promotion $4pa_1 \leftarrow 3b_1$, but recognise the inevitability of core-induced mixing between the close lying $4sa_1$ and $4pa_1$ orbitals. Hence the assignment of this feature as the first member of Series II in Table 1.

The excited states which we collect together as Series VI appear as two-photon resonances (Fig. 2) but are barely identifiable in the three-photon REMPI spectrum (Fig. 1). This is a somewhat surprising observation, since these same excited states were identified in the earlier one-photon absorption study of Tokue *et al.*⁵ Quantum defect considerations led these workers⁵ to propose that this series derives from the orbital promotion $nsa_1 \leftarrow 3b_1$, but the spectra shown in Fig. 6 clearly refute this assignment. Once again, the observation that the relative intensities of the two-photon excitations to this set of excited states are greatly diminished when carried out using circularly polarised radiation indicates that the excited states have A_1 symmetry. This rules out assignment in terms of the electronic promotion $nsa_1 \leftarrow 3b_1$ (since the resulting states would necessarily have B_1 electronic symmetry); rather, we propose that, as with Series V discussed earlier, the excited b_1 orbital has p/d hybrid character, possibly augmented by f Rydberg functions once $n > 3$. Such configuration mixing is implicit in the orbital descriptions given in Table 1, where we assign two series in terms of the promotion $nd'b_1 \leftarrow 3b_1$ notwithstanding the fact that there is only one d orbital of b_1 symmetry. Compared with higher members of this series, the first member appears both anomalously weak and broad. We take this as an indication that predissociation of this excited state is particularly efficient. Vibronic coupling between this first series member and accidentally near-resonant vibrational levels of the $60\,805\text{ cm}^{-1}$ member of Series II has been discussed previously.

The final series identified in this work, which for eventual consistency we label as Series I, appears as a sequence of three-photon resonances; none of the members we identify were reported in the earlier one-photon studies.²⁻⁵ Given

their quantum defects ($\delta \approx 1.81$ if the $62\,294\text{ cm}^{-1}$ resonance involves an excited state with $n = 5$), and the absence of these features in the two-photon REMPI spectrum, we favour assignment of this series in terms of the orbital promotion $nsa_1 \leftarrow 3b_1$. The first ($n = 4$) member of this series falls outside the range of wavelengths scanned in the present work, but has been identified previously⁵ via its one-photon absorption, *ca.* $47\,137\text{ cm}^{-1}$. Its quantum defect ($\delta \approx 1.94$) is thus a little larger than that of the higher series members, but such an observation is not uncommon for low-lying Rydberg states and is generally attributed to valence dilution of the Rydberg function. If, as is usually the case, this valence dilution imparted antibonding character to the excited orbital then this suggestion would be consistent with the non-observation of the $4sa_1 \leftarrow 3b_1$ resonance in the $1 + 1$ MPI spectrum shown in Fig. 7.

Mechanism of Fragment Ion Formation

We have been able to interpret all the observed photoelectron kinetic energy peaks in terms of REMPI resulting in the formation of just the parent ion. This, and the fact that the excitation spectra for all the molecular fragment ions show the same wavelength dependence as that of the parent ion, indicates that the observed fragment ions arise as a result of photoexcitation and subsequent fragmentation of the parent ion itself.

Recalling the electronic configuration of thiirane (2) we see that the ground-state ion will have 2B_1 symmetry. The first two excited electronic states of the ion arise as a result of removing an electron from, respectively, the $4b_2$ and $8a_1$ orbitals; conventional photoelectron spectroscopy^{11,12} shows the resulting 2B_2 and 2A_1 ion states to have vertical excitation energies (relative to the ground state) of *ca.* 2.3 and 2.8 eV. Excitation from the ground state to the first of these will be electric-dipole forbidden, but the $^2A_1 \leftarrow X\ ^2B_1$ transition should give strong one-photon absorption for wavelengths less than *ca.* 480 nm. Photoionisation studies²⁴ indicate that the absorption of one such photon will provide more than sufficient energy to cause C—H bond fission (leading to formation of $C_2H_3S^+$ fragment ions) and CH_3 elimination (*i.e.* production of HCS^+ fragment ions). Smaller fragment ions, which appear most notably in TOF spectra recorded at higher laser intensities, could arise *via* multiphoton excitation of the parent ion or following further photon absorption by the larger fragment ions (especially $C_2H_3S^+$ which is never that dominant in our ion TOF spectra).

Conclusions

This study of the vertical electronic spectrum of the thiirane molecule provides further graphic demonstration of the way in which the many complementary facets of REMPI spectroscopy can be used to unravel details of the electronic spectroscopy of small and medium-sized gas-phase molecules, even in cases where spectral congestion and/or the short excited-state lifetimes preclude observation and analysis of any rotational fine structure. Members of six Rydberg series of thiirane have been identified *via* the two- and/or three-photon resonance enhancements they provide to the mass-selected multiphoton ionisation spectrum of a jet-cooled sample of the molecule. Measurements of the kinetic energies of the photoelectrons resulting from the MPI process provide a means of determining the vibronic character of the resonance enhancing level, *e.g.* of distinguishing Rydberg origins from those involving vibrationally excited intermediate levels. The REMPI-PES studies also yield a value for the first adiabatic ionisation

potential of thiirane, $E_i = 73\,090 \pm 60\text{ cm}^{-1}$, in excellent accord with that deduced from earlier analysis of the vacuum-UV absorption spectrum.⁵ Series assignments are based on the measured quantum defects, their relative two- and three-photon transition strengths and the dependence (if any) of the two-photon transition intensities upon changing from linearly to circularly polarised photoexcitation. The present analysis suggests that, as in $H_2S^{14,15}$ many of the Rydberg orbitals have hybrid l character; it also suggests the need for some revision of all previous interpretations, both experimental²⁻⁵ and theoretical,⁶ of the electronic spectrum of the thiirane molecule.

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