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Resonance-enhanced Multiphoton Ionisation Spectroscopy of Methanethiol

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We report the first multiphoton study of excited electronic states of the methanethiol molecule. Members of four Rydberg series are identified *via* the two- and three-photon resonance enhancements they provide in the multiphoton ionisation spectrum of this molecule. Spectral analysis is aided by parallel measurements of the kinetic energies of the accompanying photoelectrons. Such studies also yield a refined value for the first ionisation limit of methanethiol: $E_i = 76\,260 \pm 40$ cm^{-1}. Detailed inspection of the photoelectron spectra obtained following REMPI *via* all but the lowest energy resonances reveal the presence of 'slower' photoelectrons, the energies of which can be interpreted if we invoke near-resonant inter-Rydberg state vibronic mixing. It is suggested that such inter-Rydberg state vibronic mixing must be rather commonplace in polyatomic systems, especially in molecules like methanethiol where symmetry imposes few restrictions on the allowed state couplings.

As part of our continuing investigations of the electronic spectroscopy of gas-phase divalent sulfide molecules[1-4] we here report the first resonance-enhanced multiphoton ionisation (REMPI) spectra of methanethiol (methyl mercaptan), CH$_3$SH. Several previous experimental[5-8] and theoretical[9,10] studies have addressed the vertical electronic spectrum of this molecule, and aspects of its photochemistry following excitation at wavelengths in the near-UV.[9,11-15] The one-photon absorption spectrum of methanethiol[9] exhibits two overlapping regions of continuous absorption in the near-UV followed, at shorter wavelengths, by many sharper vibronic features which have been assigned[5-7] in terms of Rydberg series converging to the ground-state ion. Extrapolation of these various series has yielded a value for the first ionisation potential, in reasonable accord with that determined by conventional HeI photoelectron spectroscopy[16] and by photoionisation mass spectrometry.[17]

All these earlier experimental investigations of excited states of methanethiol lying in the vacuum-UV (VUV) spectral region have relied on one-photon absorption measurements.[5-7] Spectral congestion, probably exacerbated by lifetime broadening, prevents observation of any rotational fine structure, thereby hindering unambiguous interpretation of the structured Rydberg features apparent in such spectra. Previous analyses[5-7] of the Rydberg structure exhibited by methanethiol have therefore been based largely on determination of the quantum defects, δ, of the various features, and analogy with the then-existing analyses of the vertical electronic spectrum of the related dihydride, H$_2$S.[18-20] Such comparisons have been justified by the fact that, in both molecules, the highest occupied molecular orbital in the respective ground electronic states is well approximated as the 3p$_x$ orbital of atomic sulfur. The validity of this strategy must be questioned, however, since both our own two-photon REMPI studies[3] and recent *ab initio* calculations[21] of the H$_2$S molecule have indicated the need for some revision of the traditional assignments. In particular, both of these more recent studies have served to highlight the 'atomic-like' nature of the Rydberg transitions in H$_2$S, and the propensity for odd (even) changes in the l quantum number in tran-

sitions brought about by the absorption of an odd (even) number of photons. Given these concerns, and the anticipated parallels between H$_2$S and CH$_3$SH, it seemed worthwhile to record multiphoton excitation spectra of this molecule in order to try to gain further insight into the nature and energetic ordering of its excited electronic states.

Here we report the results of a systematic study of the two- and three-photon REMPI spectra of methanethiol, supplemented by measurements of the kinetic energies of the photoelectrons accompanying the REMPI process. As in our recent REMPI study of the vertical electronic spectrum of thiirane,[4] the results from the high-resolution REMPI-photoelectron spectroscopy (REMPI–PES) experiments proved to be invaluable for establishing the vibrational properties of the various resonance-enhancing levels and, in particular, whether or not a given resonance was associated with an electronic origin. Both the two- and three-photon REMPI spectra of methanethiol 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. Members of all three series identified in the previous one-photon absorption studies[5-7] appear as both two- and three-photon MPI resonances; the present work allows identification of at least one further Rydberg series. The excited-state assignments we offer are guided primarily by quantum defect considerations. The companion REMPI–PES measurements enable refinement of the previously reported value of E_1, the first ionisation limit. More interestingly, they also reveal the presence of quite extensive vibronic mixing between the various Rydberg states and hint at a novel, 'single-shot' route to revealing large parts of the manifold of Rydberg states in such medium-sized polyatomic molecules.

Experimental

The results reported herein were obtained using two complementary apparatuses, both of which have been described previously.[4] Mass-resolved REMPI spectra of methanethiol were recorded in Bristol by focussing (fl = 200–300 mm) the output of a tunable dye laser (frequency doubled as and when necessary) into a sample of methanethiol (either the pure gas or seeded as a 10% mixture in argon, backing pressure *ca.* 1 atm in each case) expanded through a pulsed nozzle into the source region of a home-built time-of-flight (TOF) mass

spectrometer. Ions formed in the source region were subjected to two stages of acceleration prior to entering a field free drift-region and eventual detection using a channel electron multiplier. TOF spectra were obtained by feeding the amplified output from this multiplier into a fast digital oscilloscope and thence, via an IEEE interface, to a PC. MPI spectra associated with the formation of a particular ion mass were obtained by scanning the laser wavelength and collecting that part 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 simultaneous measurement of the optogalvanic spectrum of neon excited in a hollow-cathode discharge.

The REMPI–PES experiments were performed in Amsterdam using a 'magnetic bottle' spectrometer, the design and operation of which have also been detailed previously.[4] Briefly, light from an excimer pumped dye laser system or, when necessary, its second harmonic is focussed (fl = 25 mm) into the ionisation region of the electron spectrometer where it intercepts an effusive beam of pure methanethiol vapour. 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 photoelectron 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 either by concurrent kinetic energy measurements of the photoelectrons resulting from REMPI via known transitions of S atomic fragments[22] formed by parent photolysis in the source region, or by doping the methanethiol 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) three-photon resonant and (b) two-photon resonance-enhanced MPI spectra of CH_3SH obtained by monitoring the yield of ions with $m/z = 48$ as a function of excitation wavelength over the energy range 55 000–75 000 cm^{-1}. These spectra are composites of scans taken with a number of different laser dyes; in all cases the radiation was linearly polarised. As in our recent study of the vertical electronic spectrum of thiirane,[4] we have not taken any particular care about normalising the laser power either between dyes, or within the tuning range of any one dye. The emphasis in this work is on what can be learnt from the observed peak positions. We caution against placing much weight on the relative intensities of the various peaks in the displayed spectra. As in any REMPI study, the spectra in Fig. 1 will be dominated by transitions involving the less predissociated excited states but, under the prevailing experimental conditions, non-resonant MPI gives a significant background ion yield at virtually all wavelengths studied. Note, for example, the 'step' in Fig. 1(a) at excitation wavelengths ca. 526 nm (associated three-photon energy ca. 57 000 cm^{-1}), which corresponds to the long-wavelength threshold for four-photon ionisation of methanethiol. Ion
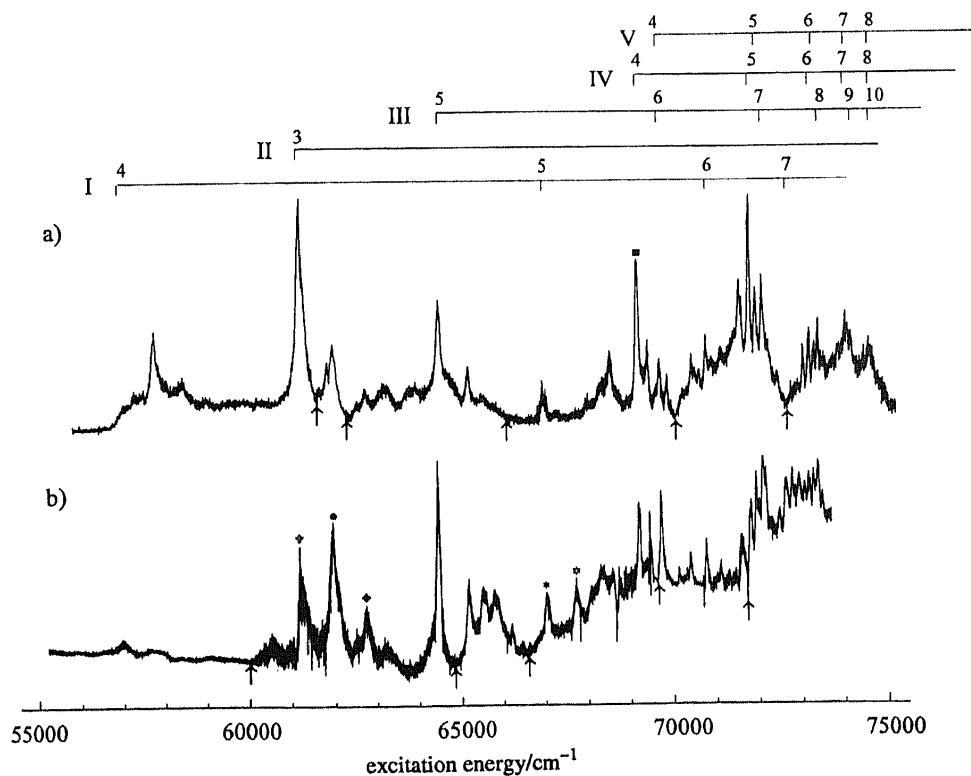

Fig. 1   (a) 3 + 1 and (b) 2 + 1 REMPI spectra of a jet-cooled sample of methanethiol over the energy range 55 000–75 000 cm^{-1} recorded using linearly polarised light and monitoring only those ions with TOF appropriate to $m/z = 48$. The displayed spectra are composites, obtained by splicing together spectra recorded using a number of different dyes. As discussed in the text, it was not possible 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. The vertical arrows arranged below the respective spectra indicate where the various scans have been joined, whilst peaks for which companion REMPI–PES are shown in Fig. 2 and 3 are designated by symbols as described in the text. Members of the various Rydberg series identified in Table 1 are indicated via the combs superimposed above the spectra. The indicated n quantum numbers are consistent with the dominant $n'l' \leftarrow 3a''$ assignments offered in Table 1.

fragmentation is a further factor affecting the relative peak intensities; as in the earlier thiirane study,[4] we find this to increase as the laser wavelength is reduced and/or as its intensity is increased. Save for the $m/z = 32$ (S^+) ion mass channel, our excitation spectra for forming each of the major fragment ions (i.e. those with $m/z = 15$, 45 and 47) show similar structure to that displayed by the parent ion (Fig. 1), implying that the molecular fragment ions we observe result from fragmentation after ionisation, and not from one-photon (or multiphoton) ionisation of neutral photofragments.

REMPI–PES

In contrast to our earlier multiphoton studies of both H_2S[1-3] and thiirane[4] we find there to be few significant differences between the $2 + 1$ and $3 + 1$ REMPI spectra of methanethiol, nor do we discern any obvious changes in the form of these spectra upon changing from linearly polarised to circularly polarised excitation. Furthermore, we can identify multiphoton resonances that match with all of the sharp features identified in the conventional one-photon absorption spectrum.[5-7] Clearly, the lowering of the molecular symmetry (from C_{2v} to C_s) on going from H_2S to methanethiol greatly relaxes any symmetry 'selection' rules that apply to these transitions. In the absence of any obvious symmetry indicators, our proposed spectral assignments are based on quantum-defect considerations, supplemented by measurements of the kinetic energies of the photoelectrons that accompany the various MPI resonances.

Fig. 2 and 3 provide illustrative examples of these photoelectron spectra. The REMPI–PES shown in Fig. 2(a), obtained following excitation at 298.5 nm ($2\tilde{\nu} = 66\,991$ cm^{-1}, marked with a * in Fig. 1), has all the characteristics of an excitation proceeding via a Rydberg origin: it is dominated by a single sharp peak, consistent with Franck–Condon diagonal ionisation from a Rydberg state with very similar geometry to that of the ground-state ion. The kinetic energy of this peak implies a value for the first ionisation potential of methanethiol, $E_i = 76\,260 \pm 40$ cm^{-1}. Both the origin assignment, and the value of E_i so derived, are in good accord with the earlier conclusions of both Price et al.[5] and Tokue et al.[7] Further confirmation of this interpretation is provided by Fig. 2(b), which shows the REMPI–PES obtained following excitation at 295.6 nm ($2\tilde{\nu} = 67\,663$ cm^{-1}, resonance marked by a ☆ in Fig. 1). This REMPI–PES is similarly dominated by a single intense peak, but its associated kinetic energy and the appearance of a weak feature some 710 cm^{-1} higher in kinetic energy suggests that the state providing the resonance enhancement at the two-photon energy is a vibrationally excited level. Such an interpretation is wholly consistent with both the past[7] and the present assignments of the parent excitation spectrum, in which this feature is viewed as the 8_0^1 (or, possible, 7_0^1, see later) vibronic transition built on the 66 991 cm^{-1} origin. Fig. 2(c) provides a further example of a REMPI–PES obtained following excitation via a Rydberg origin. In this case the resonance-enhancing level lies at the three-photon energy ($3\tilde{\nu} = 69\,159$ cm^{-1}, indicated with a ■ in Fig. 1), and ionisation involves the absorption of one further photon.

Previous analyses[5-7] have offered contradictory interpretations for the spectral region at ca. 62 000 cm^{-1}. The one-photon absorption spectrum shows a progression of features, the second of which appears most intense.[7] Our $2 + 1$ REMPI spectrum [Fig. 1(b)] shows a similar intensity distribution but the relative intensities of the corresponding features in our $3 + 1$ REMPI spectrum [Fig. 1(a)] are seriously compromised by the lower laser intensities available to us at
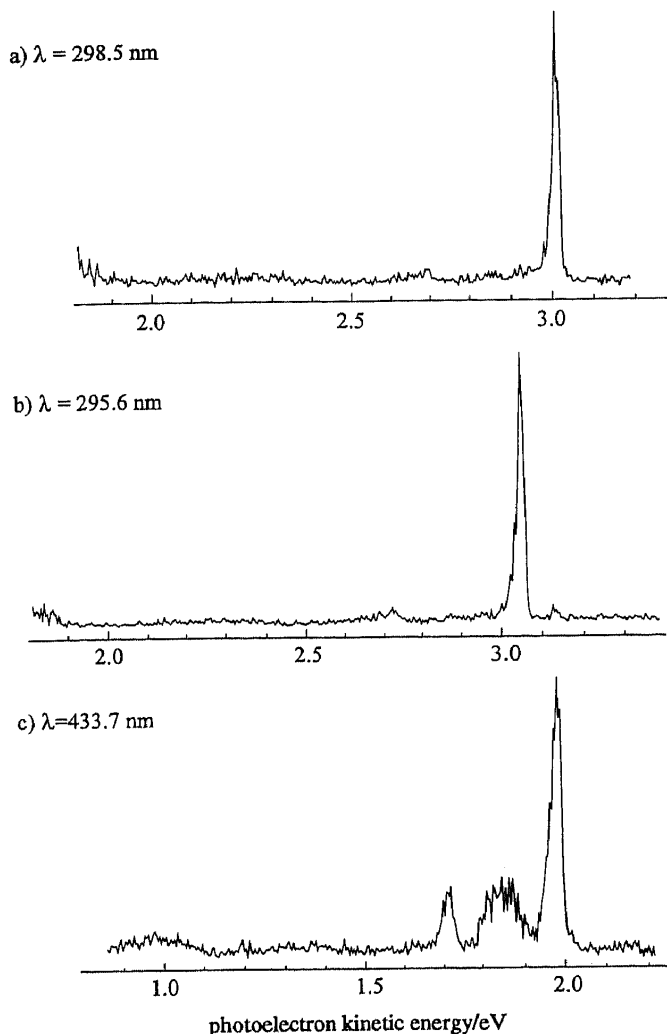

a) $\lambda = 298.5$ nm

b) $\lambda = 295.6$ nm

c) $\lambda = 433.7$ nm

photoelectron kinetic energy/eV

Fig. 2 MPI photoelectron spectra obtained following excitation of CH_3SH at: (a) 298.5 nm, where we excite a two-photon resonance ($2\tilde{\nu} = 66\,991$ cm^{-1}) involving the origin level of the state we identify as the second member of series I; (b) 295.6 nm ($2\tilde{\nu} = 67\,663$ cm^{-1}), where the kinetic energy of the dominant peak is consistent with the partner ion carrying ca. 710 cm^{-1} of internal energy, and (c) 433.7 nm, involving a three-photon resonance ($3\tilde{\nu} = 69\,159$ cm^{-1}) attributed to the origin level of the state we identify as the first member of series IV. The three spectra are plotted with a common kinetic energy dispersion, with the scales offset so that peaks corresponding to formation of the vibrationless parent ion are aligned vertically.

excitation wavelengths ca. 484 nm. Nonetheless, the companion REMPI–PES studies serve to clarify most of the previous uncertainties regarding the interpretation of this particular band system. The photoelectron kinetic energy spectra shown in Fig. 3 suggest that the 61 140 cm^{-1} resonance (✢ in Fig. 1) must be the electronic origin and that the two significant features to higher energy (● and ◆ in Fig. 1) involve, respectively, one and two quanta of excitation in a vibration the wavenumber of which is ca. 750 cm^{-1} in the resonance-enhancing state but only ca. 700 cm^{-1} in the ground state of the ion. Similar systematic REMPI–PES measurements with the laser wavelength tuned to most of the identifiable resonances in Fig. 1 have led to the assignments listed in Table 1. Discussions of the electronic promotions responsible for these various features, and of the nature of the vibrational motions observed to be active in these spectra, are reserved until later.

Closer inspection of the REMPI–PES displayed in Fig. 3 reveals an additional, slower peak. REMPI–PES taken whilst exciting via higher wave number bands were observed to exhibit more than one such 'slow' peak: Fig. 4 provides one such illustrative example, and hints at an explanation. The
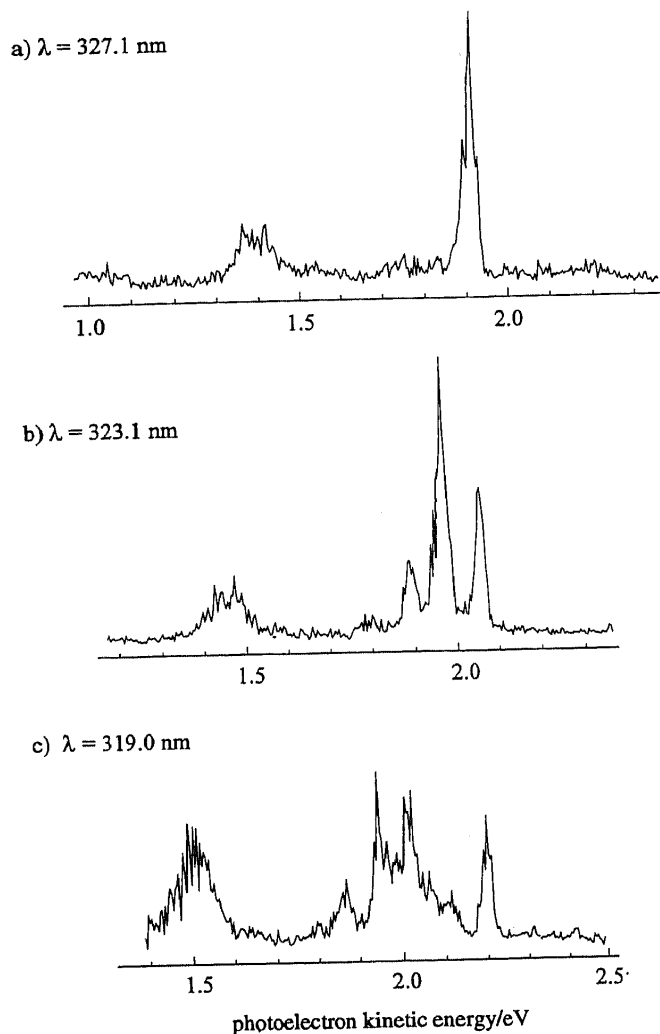
a) λ = 327.1 nm

1.0   1.5   2.0

b) λ = 323.1 nm

1.5   2.0

c) λ = 319.0 nm

1.5   2.0   2.5·

photoelectron kinetic energy/eV

Fig. 3 Photoelectron spectra obtained following two-photon resonance enhanced MPI of CH_3SH at: (a) 327.1 nm ($2\tilde{v} = 61\,140$ cm^{-1}), (b) 323.1 nm ($2\tilde{v} = 61\,897$ cm^{-1}) and (c) 319.0 nm ($2\tilde{v} = 62\,697$ cm^{-1}). These serve to demonstrate that the $61\,140$ cm^{-1} feature is an electronic origin, and indicate the vibrational content of the two higher-energy resonances. Note also the 'slower' photoelectron peak which we attribute to vibronic mixing with near-resonant vibrationally excited levels of the Rydberg state with origin at $56\,902$ cm^{-1}. As in Fig. 2, the spectra are displayed with the same kinetic energy dispersion, with the scales offset so that peaks corresponding to formation of the vibrationless parent ion are aligned vertically.

REMPI–PES shown in Fig. 4 involved four-photon ionisation, resonance-enhanced at the three-photon energy by the electronic origin at $66\,991$ cm^{-1}. The sharp peak in the photoelectron kinetic energy spectrum at 1.619 eV is entirely consistent with this interpretation. Three slower photoelectron peaks are also evident in Fig. 4. Consider the peak centred around 1.30 eV. Knowing E_1, simple energy conservation requires that the partner ions be formed with an internal energy of ca. 0.32 eV (2580 cm^{-1}), an energy that closely matches the energy separation of the $66\,991$ cm^{-1} and $64\,413$ cm^{-1} origins. As Fig. 4 shows, the energy separations between the 1.619 eV feature and the other two photoelectron peaks also closely correspond to Rydberg origin separations identified in this work. (Note that the $56\,902$ cm^{-1} origin does not show as a three-photon resonance because, at these energies, ionisation is much less probable, necessarily involving a five-photon absorption process). We interpret these observations in terms of near-resonant vibronic mixing between the Rydberg origin (which, in the language of radiationless transition theory, would here constitute the zero-order 'bright' state) and the various manifolds of 'dark'
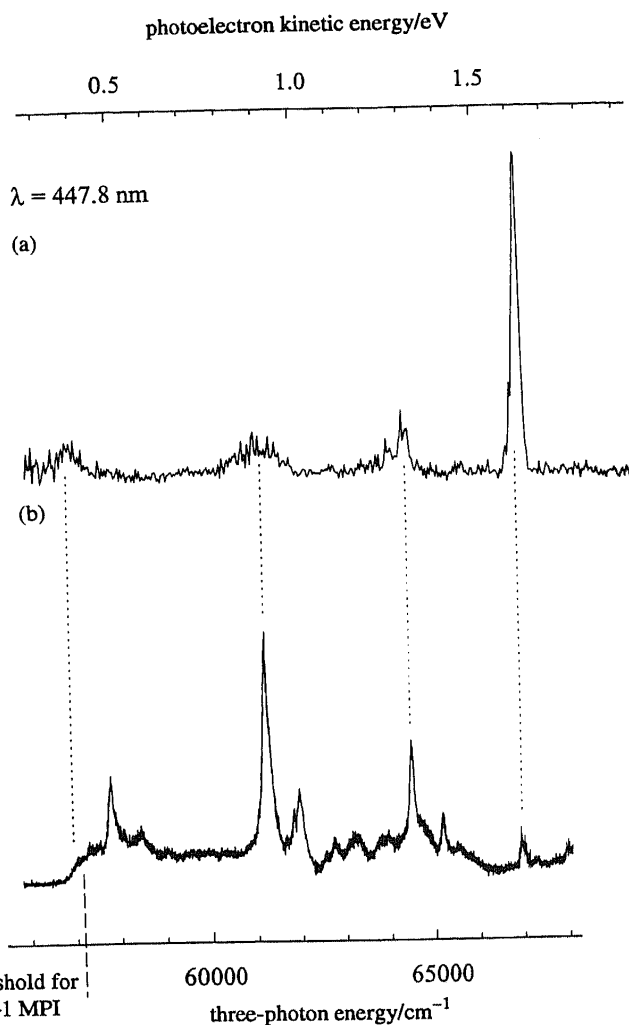
photoelectron kinetic energy/eV

0.5   1.0   1.5

λ = 447.8 nm

(a)

(b)

threshold for
·3+1 MPI

60000   65000

three-photon energy/cm^{-1}

Fig. 4 (a) REMPI–PES taken following excitation at: (a) 447.8 nm, where ionisation proceeds via a three-photon resonance ($3\tilde{v} = 66\,991$ cm^{-1}) involving the origin level of the second ($n = 5$) member of Series I, together with (b) the relevant portion of the three-photon REMPI spectrum of methanethiol, displayed with the same energy dispersion. Note how the various 'slower' photoelectron peaks in (a) align with the identified origin transitions in the parent excitation spectrum (b). (Note that the $56\,902$ cm^{-1} origin does not appear as a three-photon resonance in (b) because ionisation at this wavelength requires the absorption of a total of five photons).

vibrational levels built on Rydberg states whose origins lie lower in energy. Given the structural similarity of the Rydberg states and the ion, Franck–Condon considerations will favour near-preservation of the vibrational energy upon ionisation. Hence the close similarities between the observed energy separations of the photoelectron peaks and the corresponding Rydberg origins (Fig. 4). Note that, in principle at least, this information on the energies of the various Rydberg origins could be derived from measurement of the kinetic energies of the photoelectrons resulting from a 'single-shot' REMPI experiment.

The REMPI–PES shown in Fig. 3(b) and (c) provide further support for this interpretation. Consider the former, which we have interpreted as showing that a Rydberg level carrying one quantum of a ca. 750 cm^{-1} mode provides the dominant resonance enhancement. Energy conservation dictates that the parent ions partnering the slower photoelectrons (with kinetic energies centred around 1.45 eV) must have an internal (presumed vibrational) energy of ca. 5030 cm^{-1}, a value in almost quantitative accord with the separation between the two-photon excitation energy and the $56\,902$ cm^{-1} Rydberg origin. Once again, this is most readily explained by invoking vibronic mixing between the Series II

Table 1 Wavenumbers, effective quantum numbers (n^*) and proposed assignments of the methanethiol resonances observed in the present multiphoton study

$\tilde{\nu}$/cm^{-1}	n^*	proposed assignment	one-photon VUV$^{a(b)}$	$\tilde{\nu}$/cm^{-1}	n^*	proposed assignment	one-photon VUV$^{a(b)}$
	Series I	n‘p’←3a″			Series II	n‘d’←3a″	
56 902	2.40	origin	56 902	61 140	2.69	origin	(61 144)
57 674		+772 cm^{-1}		61 897		+757 cm^{-1}	
66 991	3.44	origin	66 943 (66 968)	62 697		+1557 cm^{-1}	
67 663		+672 cm^{-1}		63 188		+2048 cm^{-1}	
68 075		+1084 cm^{-1}					
68 297		+1306 cm^{-1}					
68 544		+1553 cm^{-1}					
70 700	4.44	origin	70 641 (70 650)				
72 591	5.44	origin					
	Series III	n‘s’←3a″			Series IV	n‘d’←3a″	
64 413	3.05	origin	64 367	69 159	3.93	origin	69 109 (69 124)
65 110		+697 cm^{-1}		71 744	4.93	origin	71 654 (71 660)
65 477		+1064 cm^{-1}		72 435		+691 cm^{-1}	
65 763		+1350 cm^{-1}		73 104	5.93	origin	73 046 (73 038)
69 760	4.06	origin		73 966	6.93	origin	73 877 (73 882)
70 339		+669 cm^{-1}		74 496	7.93	origin	
70 700		+1030 cm^{-1}					
71 050		+1380 cm^{-1}					
72 042	5.08	origin					
72 726		+684 cm^{-1}					
73 307	6.08	origin					
74 100	7.08	origin					
	Series V	n‘f’←3a″					
69 399	4.00	origin					
71 875	5.00	origin					
73 202	6.00	origin					
74 022	7.00	origin					

^{a} Ref. 7; value in parentheses, ref. 5.

Rydberg level (adopting the nomenclature of Table 1) carrying one quantum of the ca. 750 cm^{-1} mode and some or all of those accidentally near-resonant excited vibronic levels associated with the first member of our Series I. These latter levels have internal energies of ca. 5030 cm^{-1} which, by Franck–Condon arguments, we would expect (and indeed observe) to be largely conserved upon ionisation. Evidence for similar inter-Rydberg state vibronic mixing has recently been reported for methyl iodide[23] and, to a far greater degree, for azulene[24] and pyrazine.[25] Companion studies in our own groups[26] reveal similar mixing amongst the Rydberg states of dimethylsulfide, leading us to suggest that such behaviour will in fact become recognised as the norm in medium (and large) polyatomics, especially those like methanethiol where the vibrational state density is neither too sparse nor too high and where symmetry imposes few restrictions on the possible vibronic mixing.

Assigning the Multiphoton Resonances

We now return to consider the assignment of the various features appearing in the REMPI excitation spectra (Fig. 1). In common with previous workers, we attempt to assign the observed features as members of Rydberg series converging to the first ionisation potential, $E_i = 76\,260$ cm^{-1}. Wavenumbers corresponding to the measured band maxima ($\tilde{\nu}$) are listed in Table 1 together with their associated n^* values, which have been calculated using the relationship

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

where R is the Rydberg constant (109 737 cm^{-1}), $n^* = (n - \delta)$ and δ is the quantum defect. For completeness, we also list the major peaks identified in the one-photon absorption studies of Price *et al.*[5] and Tokue *et al.*[7] The resulting

quantum defects suggest assignment of four, possibly five, separate Rydberg series, including the three series identified previously.[5-7] All features are discernible as both two- and three-photon resonances.

The electronic configuration of ground-state methanethiol is normally written as

$$(2a'')^2(9a')^2(10a')^2(3a'')^2; \quad \tilde{X}\,{}^1A', \qquad (2)$$
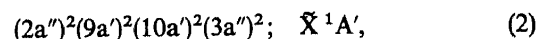
with the highest occupied 3a″ orbital being essentially non-bonding (being dominated by the 3p$_x$ orbital of atomic sulfur, directed perpendicular to the plane containing the C—S—H framework).[7,9,10] Promoting one 3a″ electron to higher nl Rydberg orbitals can be expected to give rise to one ‘s’ ($l = 0$) series involving states of ${}^1A''$ electronic symmetry with principal quantum number $n \geqslant 4$, three ‘p’-series (two of ${}^1A''$ symmetry, the other ${}^1A'$, all with $n \geqslant 4$), five ‘d’-series (three ${}^1A''$, two ${}^1A'$, with $n \geqslant 3$), seven ‘f’-series (four ${}^1A''$, three ${}^1A'$, $n \geqslant 4$) etc. As in our recent work on the vertical electronic spectrum of thiirane[4] the parentheses are included as a reminder that configuration mixing may render l an approximate label, though not invalidate the overall state count. Analogy with atomic sulfur and with H$_2$S suggests that ‘pure’ l series will exhibit quantum defects around 2.0 (‘s’-series), 1.6 (‘p’) and 0 (for ‘d’, ‘f’ and higher l functions).[1-3,22] Such expectations led to the assignment of one s ($\delta = 2.05$), one p ($\delta = 1.55$) and one d ($\delta = 0.32$) Rydberg series in the earlier one-photon studies of methanethiol.[5-7]

The progression we label Series I in both Fig. 1 and Table 1, which has an associated quantum defect $\delta \approx 1.6$ if we assume that the first (56 902 cm^{-1}) member involves an excited orbital with $n = 4$, has been identified previously in one-photon absorption, and we see no reason to contradict the earlier suggestions[5-7] that this series arises as a result of

electron promotion from the highest occupied 3a″ orbital to Rydberg orbitals that have predominant p ($l = 1$) character. Note that, in contrast to our previous findings with related (but more symmetric) sulfur-containing species like H_2S[1-3] and thiirane,[4] the fact that this series appears quite strongly in one-photon absorption and our observation of three-photon resonances associated with these excited states serves to emphasise the limited relevance of the 'atomic' description in interpreting Rydberg transition strengths in this molecule. The present work provides little, if any, additional insight into the nature of this particular series, though neither its strength in the one-photon absorption spectrum, nor the vibronic simplicity of its associated REMPI–PE spectra (see Fig. 2 for REMPI–PE spectra excited *via* its $n = 5$ member) sit entirely comfortably with the proposal of Rauk and Collins[9] that the $n = 4$ member (at least) involves an orbital with significant antibonding valence character.

The identification and (partial) interpretation of the series we label III, IV and V does not appear particularly controversial, so we consider them next. All three exhibit near-integer quantum defects, suggesting that they should be viewed in terms of excitation to Rydberg orbitals with predominant s, d or f character. As Table 1 shows, several members of our Series III and IV have also been identified in one-photon absorption, though Tokue et al.[7] chose to subdivide them somewhat differently. Most striking, however, is our observation of the progression we label Series V, which appears to have no counterpart in the one-photon spectrum and exhibits term values and quantum defects entirely consistent with the assignment $n'f' \leftarrow 3a''$. The observation of one or more such series in the REMPI spectrum of this molecule should come as little surprise: similar series have been identified in recent multiphoton studies of both H_2S[3] and thiirane.[4] Previous workers[5-7] have chosen to assign the 64 413 cm^{-1} feature in terms of the 5s (rather than a 3d) Rydberg excitation, though either of these assignments would be plausible on quantum-defect grounds. However if, as in Table 1, we choose to assign Series III and IV in terms of, respectively, $n's' \leftarrow 3a''$ and $n'd' \leftarrow 3a''$ electron promotions it then follows that there must be a 'missing' first member of each series. Theory,[9-12] and analogy with H_2S,[17-21] suggests that the nominal 4's' $\leftarrow$ 3a″ Rydberg promotion in methanethiol has a substantial valence contribution and is responsible for the strong continuous absorption centred around 210 nm. This accounts for the absent first member of our Series III, but still leaves a question mark hanging over Series IV.

At this point it is worth recalling the set of vibronic features that we have labelled as the one (and apparently only) member of Series II, the interpretation of which has caused problems in all previous analyses.[5-7] The associated REMPI–PE spectra (Fig. 3) are most readily understandable if we view the REMPI excitation spectrum in terms of one dominant vibrational progression (involving a *ca.* 750 cm^{-1} mode) built on a single electronic origin (at 61 140 cm^{-1}). This excitation differs from all other Rydberg transitions identified in the vertical electronic spectrum of methanethiol in as much that it is not dominated by its origin band. {This can be seen most clearly in the present 2 + 1 REMPI spectrum [Fig. 1(b)] and in the one-photon absorption spectrum shown in Fig. 2 of ref. 7; variations in the dye laser output energy seriously distort the relative intensities of these vibronic features in the 3 + 1 REMPI spectrum shown in Fig. 1(a)}. Rydberg–valence mixing provides the most obvious explanation for the observed vibronic activity. Such mixing often causes the electronic origin to appear to lower energy than would be predicted by eqn. (1) (which assumes that the excited orbital is a pure Rydberg orbital). Thus, given its term value, its presumed valence contamination, and the absence

of any higher members that obviously fit as part of Series II, it is tempting to speculate that the 61 140 cm^{-1} feature could actually be the 'missing' first member of the progression we label Series IV.

Finally, in this section, we comment briefly on the nature of the excited state (and ion) vibrations that we observe to be active. Tokue et al.[7] have reported *ab initio* frequencies for the twelve normal mode vibrations in both the ground-state neutral and the ion. As usual, these calculations tend to overestimate the absolute frequencies, but should be fairly reliable when it comes to predicting which modes will be most affected by ionisation. Of the totally symmetric modes, Tokue et al.[7] predict that ionisation will most affect the frequency of the v_8 (C—S stretching) vibration and, consistent with this prediction, both the REMPI spectra and the photoelectron spectra show several *ca.* 700–750 cm^{-1} intervals which we associate with this mode. Franck–Condon considerations suggest that this must be the mode most apparent in the parent absorption and REMPI spectra, though previous analyses[7] have emphasised how difficult it is to distinguish activity in the v_8 and v_7 (C—S—H bending) modes in such low-resolution spectra purely on energetic grounds. Two other intervals are observed to feature with some regularity, both in the parent excitation spectrum and in the REMPI–PE spectra: one *ca.* 1050 cm^{-1}, the other *ca.* 1350 cm^{-1} (see Table 1). The calculations[7] suggest that these are most likely associated with the v_6 (predominantly CH_3 rocking) and v_5 (CH_3 symmetric bending) modes.

Conclusion

This study of the vertical electronic spectrum of methanethiol provides further illustration of the way in which REMPI spectroscopy, allied with the capability of recording the associated REMPI–PE spectra, can complement and extend conclusions drawn from traditional one-photon absorption spectroscopy. The present work provides a refined value of the first ionisation potential of CH_3SH, $E_1 = 76 260 \pm 40$ cm^{-1}, and allows identification of members of (at least) four Rydberg series converging to this limit. Many of these features have been identified in previous one-photon absorption studies of this molecule;[7-9] the present study suggests the need for some reassignment of series members with near-integer quantum defect and also reveals one hitherto unobserved series which we associate with electron promotion from the highest occupied (3a″) orbital to Rydberg orbitals with predominant f ($l = 3$) character. Finally, careful inspection of the PE spectra obtained following REMPI *via* all but the lowest-energy resonances show one or more 'slower' peaks which we interpret in terms of inter-Rydberg state vibronic mixing. We suggest that such observations will turn out to be quite commonplace in polyatomic systems with vibrational state densities comparable to (or greater than) that of methanethiol, especially in molecules like methanethiol where symmetry imposes few restrictions on the allowed state couplings.

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