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DOI

[10.1039/ft9959103339](https://doi.org/10.1039/ft9959103339)

Publication date

1995

Published in

Journal of the Chemical Society. Faraday transactions

[Link to publication](#)

Citation for published version (APA):

Morgan, R. A., Orr-Ewing, A. J., Ashfold, M. N. R., Buma, W. J., Wales, N. P. L., & de Lange, C. A. (1995). Resonance enhanced multiphoton ionisation spectroscopy of dimethyl sulfide. *Journal of the Chemical Society. Faraday transactions*, 91, 3339-3346.
<https://doi.org/10.1039/ft9959103339>

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Resonance Enhanced Multiphoton Ionisation Spectroscopy of Dimethyl Sulfide

Ross A. Morgan, Andrew J. Orr-Ewing and Michael N. R. Ashfold
School of Chemistry, University of Bristol, UK BS8 1TS

Wybren Jan Buma, Nicolas P. L. Wales and Cornelis A. de Lange
Laboratory for Physical Chemistry, University of Amsterdam, Nieuwe Achtergracht 127, 1018 WS
Amsterdam, The Netherlands

We report the first multiphoton study of the electronic spectrum of the dimethyl sulfide molecule. The interpretation we present is based on analysis of the two- and three-photon resonance enhanced multiphoton ionisation (REMPI) spectra and measurements of the kinetic energies of the photoelectrons resulting from the REMPI process. Members of four (possibly five) Rydberg series are identified and a refined value of the first ionisation limit of dimethyl sulfide is obtained: $E_i = 8.710 \pm 0.005$ eV ($70\,250 \pm 40$ cm⁻¹). As in our previous study of the related divalent sulfide methanethiol, we detect the presence of slower electrons in the photoelectron spectra which can be interpreted in terms of near resonant inter-Rydberg state vibronic mixing.

REMPI spectroscopic techniques are proving to be ever more useful as a method for determining the nature of the higher excited electronic states, most notably Rydberg states, of small and medium-sized polyatomic molecules. This paper is concerned with the molecule dimethyl sulfide (DMS, H₃CSCH₃), a major natural source of tropospheric sulfur,¹ and represents a natural extension of our multiphoton investigations of other small divalent sulfides,³ e.g. hydrogen sulfide,^{2–4} methanethiol⁵ and thiirane.⁶ Once again we demonstrate how, through a combination of wavelength-resolved MPI spectroscopy and measurement of the kinetic energies of the photoelectrons accompanying the MPI process, it is possible to obtain a much improved interpretation of the excited electronic states of the target molecule. Previous experimental studies^{7–11} of the electronic spectrum of DMS have all involved one-photon ultraviolet (UV) and vacuum ultraviolet (VUV) absorption; spectral interpretation has been based largely on comparison with the simplest divalent sulfide, hydrogen sulfide.¹² Such comparisons have been justified by the fact that both molecules have the same C_{2v} backbone and, in both cases, the highest occupied molecular orbital in the respective ground electronic states is non-bonding, with the dominant contribution coming from the 3p_x orbital of atomic sulfur. Assignment of the Rydberg structure observed in absorption has thus far been based largely on interpretation of the quantum defects associated with the individual features and comparison with the then existing analyses of the electronic spectrum of H₂S, but unambiguous assignment is hampered by the lack of any observable rotational fine structure. However, given the findings of recent *ab initio* calculations of the pattern and identity of the excited electronic states of H₂S¹³ and our own multiphoton investigations of the Rydberg states of H₂S^{2–4} and the related divalent sulfides methanethiol⁵ and thiirane,⁶ it has become increasingly clear that there is likely to be a need for some revision of the traditional assignments. The more recent studies^{2–4,13} have highlighted the 'atomic-like' nature of the transitions to Rydberg states in H₂S, and the marked propensity for odd (even) changes in the *l* quantum number in the case of transitions induced using an odd (even) number of photons. Our recent studies of larger divalent sulfides such as the lower-symmetry species methanethiol⁵ and the strained three-membered heterocycle thiirane⁶ might indicate that increasing molecular complexity allows some (partial) relaxation of these Δl propensities, a hypothesis which the present study of DMS allows us to test further. The one-

photon absorption spectrum of DMS shows a region of weak diffuse absorption the long wavelength onset for which is *ca.* 230 nm followed, to shorter wavelengths, by a broad intense feature centred at *ca.* 203 nm and, in the VUV, by a number of sharp vibronic features which can be arranged into Rydberg series converging to the first ionisation potential. Extrapolation of the more prominent series yields a value of 8.706 ± 0.010 eV⁹ for this limit, a value in good agreement with that determined by conventional HeI photoelectron (PE) spectroscopy.¹⁴

Here we report a systematic study of the two- and three-photon REMPI spectra of a jet-cooled sample of dimethyl sulfide. Numerous vibronic features are apparent in each spectrum, though few of these are common to both, thus highlighting, once again, the influence of the Δl propensity rule in establishing multiphoton transition intensities in the electronic spectra of these sulfide molecules. Many of these resonances can be assigned as members of well defined Rydberg series converging to the ground state of the molecular ion. As in our recent REMPI studies of methanethiol⁵ and thiirane,⁶ 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.

Experimental

The results reported in this paper were recorded using complementary apparatuses in Bristol and Amsterdam. Mass-resolved REMPI spectra of DMS were recorded in Bristol by expanding the parent gas (Aldrich, 99 + %, stagnation pressure *ca.* 1 atm) into the source region of a home-built time-of-flight (TOF) mass spectrometer.^{4,15} Here it was intercepted by the focussed output of a tunable dye laser (frequency doubled as and when necessary); the resulting ions were subjected to two stages of acceleration prior to entering a field-free drift region and eventual detection using a channel electron multiplier. As before,⁴ TOF spectra were obtained by passing the amplified output from this multiplier into a fast digital oscilloscope and, *via* an IEEE interface, to a PC. REMPI spectra associated with any chosen *m/z* ratio were recorded by scanning the laser wavelength and collecting just that part of the total ion signal that falls within the user-selected narrow time window spanning the appropriate TOF. Wavelength calibration, in the visible, involved simultaneous

measurement of the optogalvanic spectrum of neon excited in a hollow cathode discharge.

The complementary REMPI-PE spectra were recorded in Amsterdam using a 'magnetic bottle' spectrometer.^{16,17} Tunable dye laser radiation (here also frequency doubled as and when necessary) was focussed into the ionisation region of the electron spectrometer where it intercepts an effusive beam of pure DMS vapour. Photoelectrons resulting from each laser pulse were 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 resulting signal was pre-amplified and passed to a transient digitiser, which was interfaced to a PC. A photoelectron spectrum was constructed by successively stepping up the retarding voltage on a grid in the flight tube, and transforming just the long time (and highest resolution) part of the TOF spectrum. Thus it was possible to achieve an energy resolution of *ca.* 15 meV (FWHM) at all photoelectron 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 fragments¹⁸ resulting from precursor photolysis in the source region, or by doping the DMS 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 shows the composite two-photon REMPI spectrum of DMS recorded using linearly polarised light in the wave-

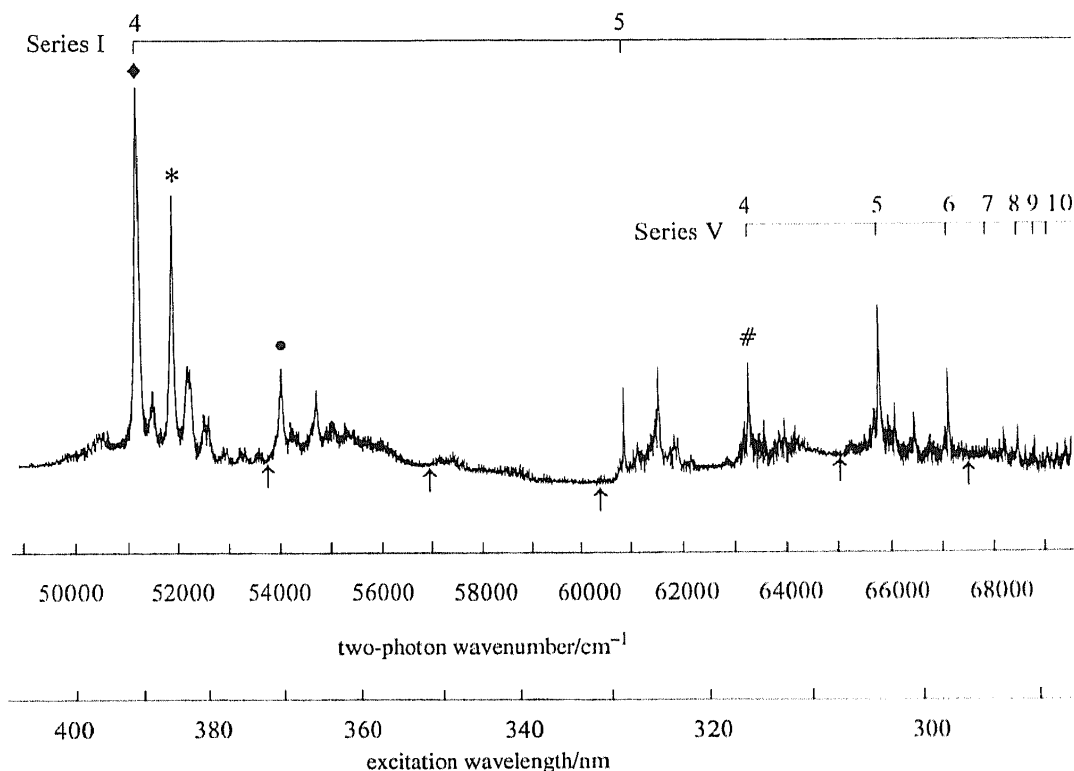


Fig. 1 2 + 1 REMPI spectrum of jet-cooled DMS recorded over the wavelength range 287–409 nm using linearly polarised laser radiation and monitoring only those ions with TOFs appropriate for m/z 62. The displayed spectrum is a composite, obtained by splicing together spectra recorded using several different laser dyes. The tuning ranges covered with each dye are indicated by the vertical arrows arranged below the spectrum. The relative intensities of the features appearing in each of these constituent spectra have not been corrected for the wavelength dependence of the dye laser output energy, nor have we taken any particular care to ensure correct normalisation of the relative intensities of features appearing within neighbouring tuning ranges. Members of Rydberg series that appear clearly as two 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. Spectral features for which we show the associated REMPI-PE spectra are indicated with symbols: ◆, * etc. (see text for further details).

length region 409–287 nm and monitoring just that fraction of the total ion signal associated with the parent ion (m/z 62). Fig. 2 shows the corresponding three-photon REMPI spectrum, recorded using excitation wavelengths in the range 568–429 nm. These spectra were recorded using a number of different laser dyes; we have not paid particular attention to normalising the laser power either between dyes, or within the range of any one dye. This study is primarily concerned with peak positions, and whether a particular excited state provides resonance enhancement at the energy corresponding to two and/or three absorbed photons. The relative peak intensities will also be affected by ion fragmentation. Fig. 3 illustrates how the relative intensities of the various mass peaks in the TOF spectra are seen to vary with excitation wavelength (fragmentation becomes more prevalent at shorter wavelengths) and with the incident pulse energy. All peaks save for the S⁺ (m/z 32) ion peak exhibit similar wavelength resolved excitation spectra as the parent ion, thus implying that most (if not all) of the observed fragmentation occurs after ionisation.

REMPI-PE Spectra

Measurements of the kinetic energies of the photoelectrons associated with the REMPI process can be used to obtain an accurate value for the first ionisation potential of DMS. Fig. 4 shows a representative set of REMPI-PE spectra where, in each case, the electrons arise from a two-photon resonant three-photon ionisation process. Each is dominated by a single peak consistent with the final one-photon ionisation step from the resonance-enhancing Rydberg state involving a $\Delta v = 0$ transition, as expected if the Rydberg state has an equilibrium geometry very similar to that of the ground-state

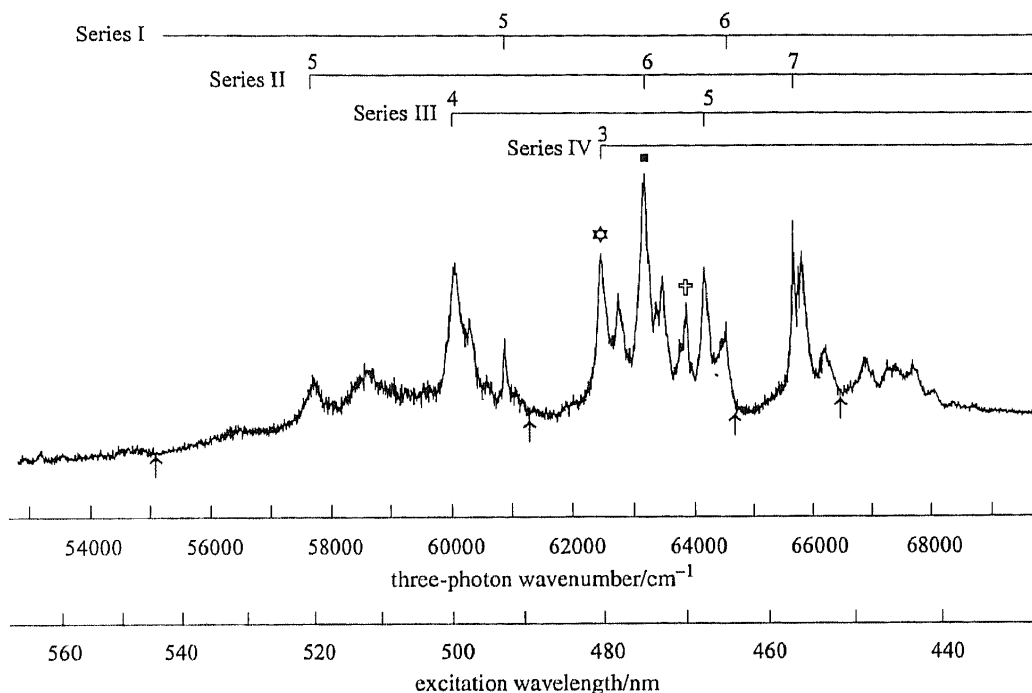


Fig. 2 3 + 1 REMPI spectrum of DMS recorded over the wavelength range 429–568 nm using linearly polarised light and monitoring only those ions with TOFs appropriate for the parent ion (m/z 62). As in Fig. 1, the displayed spectrum is a composite, and the same comments apply. Members of Rydberg series clearly identified as three-photon resonances are indicated *via* the combs superimposed over the spectrum.

ion. Consider the spectrum shown in Fig. 4(a), obtained following excitation at 390.7 nm ($2\tilde{\nu} = 51\,184\text{ cm}^{-1}$, indicated with a \blacklozenge in Fig. 1). The dominant peak in this spectrum is centred at an energy of 0.809 eV (6525 cm^{-1}). The absence of any obvious faster electrons leads to the suggestion that the ion is being formed in its vibrationless level and thus, given the assumed propensity for $\Delta v = 0$ transitions in the final

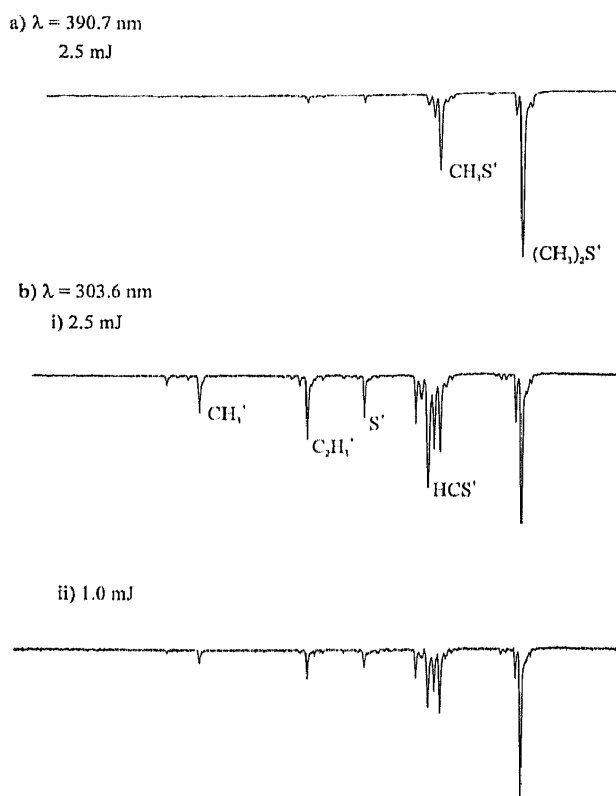


Fig. 3 Ion TOF spectrum obtained following REMPI of DMS at (a) 390.7 and (b) 303.6 nm using pulse energies of (a) and (b, i) 2.5 mJ and (b, ii) 1.0 mJ. These provide clear illustration of the increased fragmentation that accompanies use with higher incident light intensities and/or shorter excitation wavelengths.

one-photon ionisation step, that the resonance enhancement also involves an electronic origin. The appearance of this MPI resonance in the wavelength-resolved excitation spectrum (Fig. 1) and, in particular, the lack of any comparable features at lower energy is wholly consistent with such a suggestion. Given this assumption, we can use the measured photoelectron kinetic energy to obtain a value for the first adiabatic E_i : $8.710 \pm 0.005\text{ eV}$ ($70\,250 \pm 40\text{ cm}^{-1}$), in very good accord with values obtained from previous extrapolations of Rydberg series identified in the one-photon absorption spectrum^{9–11} and by traditional HeI PES.¹⁴ Analogous kinetic energy measurements of photoelectrons formed when exciting *via* other Rydberg origins [see *e.g.* Fig. 5(a) and (b) and 6] provide further confirmation of the correctness of this value for the first E_i of DMS. Neither of the other two photoelectron spectra shown in Fig. 4 [Fig. 4(b) and (c), obtained following excitation at 385.5 nm ($2\tilde{\nu} = 51\,883\text{ cm}^{-1}$, identified by the \star in Fig. 1) and 370.2 nm ($2\tilde{\nu} = 54\,018\text{ cm}^{-1}$, \bullet in Fig. 1), respectively] show a peak at an energy consistent with formation of vibrationless ions. Rather, the dominant peak in both of these two examples appears at lower kinetic energies thus suggesting that, in each case, a vibrationally excited level provides the resonance enhancement at the two-photon energy and that this vibrational energy is preserved upon ionisation. The former REMPI-PE spectrum [Fig. 4(b)] indicates that the ions are formed with *ca.* 88 meV (710 cm^{-1}) of internal energy, a value which we associate with a single quantum of the C—S stretching vibration, ν_6 . The latter [Fig. 4(c)] shows the companion ions to be formed with *ca.* 2840 cm^{-1} of vibrational energy, a value that matches closely with the separation between this $54\,018\text{ cm}^{-1}$ resonance and the origin identified in the 2 + 1 REMPI spectrum at $51\,184\text{ cm}^{-1}$. Once again, the simplicity of the REMPI-PE spectrum suggests that we are concerned with a level involving just one quantum of a single vibrational mode which, on energy grounds, we assume to be one or other of the totally symmetric C—H stretching modes ν_1 and ν_2 .^{9,19}

As a further example of the way in which REMPI-PES can aid assignment of wavelength-resolved REMPI spectra, consider the group of three-photon resonances in the region

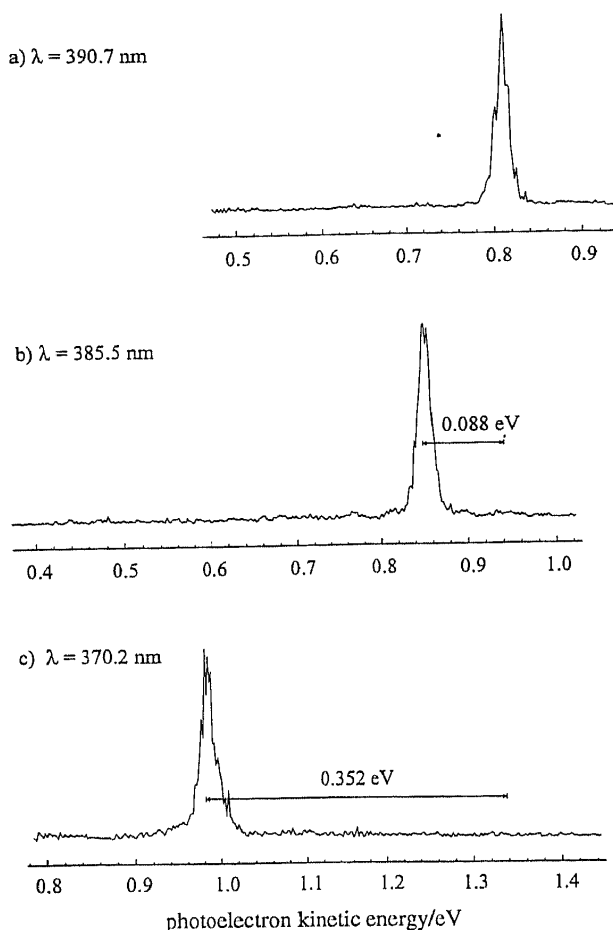


Fig. 4 REMPI-PE spectra of DMS obtained following excitation at: (a) 390.7 nm ($2\bar{\nu} = 51\,184\text{ cm}^{-1}$), where we excite a two-photon resonance involving the origin level of the state we identify as the first member of Series I; (b) 385.5 nm ($2\bar{\nu} = 51\,883\text{ cm}^{-1}$), where the kinetic energy of the dominant peak is consistent with the partner ion being formed with 88 meV (710 cm^{-1}) of internal energy and (c) 370.2 nm ($2\bar{\nu} = 54\,018\text{ cm}^{-1}$), where the dominant peak indicates that the partner ion carries 352 meV (2840 cm^{-1}) of internal energy. The spectra are displayed with the same kinetic energy dispersion, with the scales offset so that the energies appropriate for formation of the vibrationless parent ion are aligned vertically.

$62\,000\text{--}65\,000\text{ cm}^{-1}$. All these features are observed as three-photon resonances only; they do not appear in the $2 + 1$ REMPI spectrum (Fig. 1) or in the previously reported one-photon absorption spectra.^{9–11} These all appear reasonably strongly but can they all be assigned as electronic origin transitions? Examples of PE spectra obtained following MPI *via* three of these resonances are shown in Fig. 5. The $3 + 1$ REMPI-PE spectra shown in Fig. 5(a) and (b) were recorded at excitation wavelengths of 479.9 nm ($3\bar{\nu} = 62\,510\text{ cm}^{-1}$, ☆ in Fig. 2) and 474.7 nm ($3\bar{\nu} = 63\,204\text{ cm}^{-1}$, ■ in Fig. 2), respectively. In both cases the PE spectrum is dominated by a peak which appears at an energy consistent with the formation of vibrationless ions, indicating that these two features are, indeed, origin transitions. In contrast, the REMPI-PE spectrum shown in Fig. 5(c), obtained following excitation at 469.6 nm ($3\bar{\nu} = 63\,880\text{ cm}^{-1}$, ♣ in Fig. 2), shows only a very small peak at the kinetic energy appropriate for formation of ions in their vibrational ground state; the energy of the dominant peak implies that the ion is formed with *ca.* 108 meV (870 cm^{-1}) of vibrational energy.

Closer inspection of the REMPI-PE spectra displayed in Fig. 5 reveals additional, slower peaks. Fig. 6 provides a further illustration of a REMPI-PE spectrum exhibiting these anomalous 'slower' electrons, here involving a three-photon ionisation, resonance enhanced at the two-photon

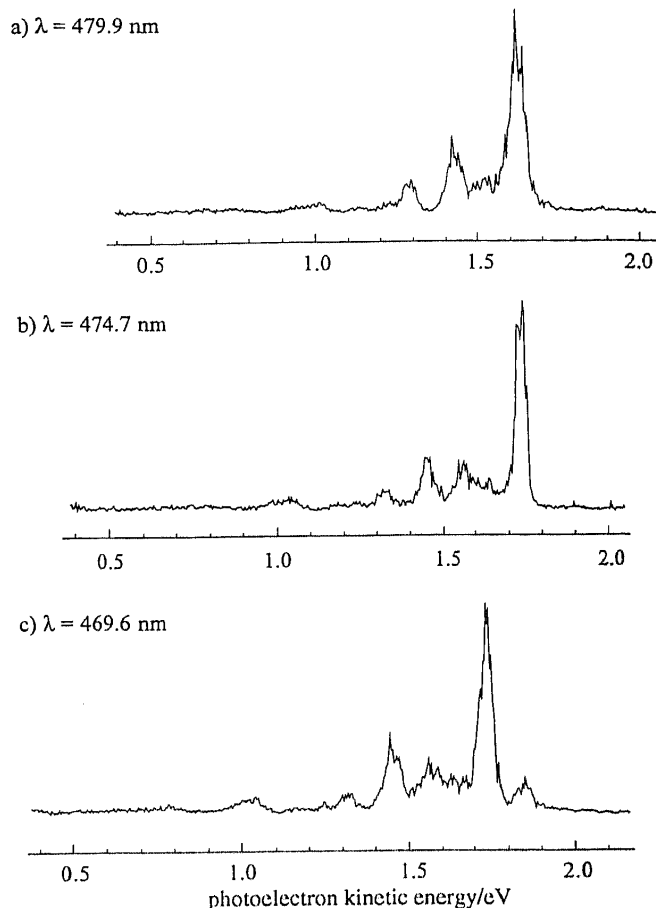


Fig. 5 REMPI-PE spectra of DMS observed following excitation at (a) 479.9 nm ($3\bar{\nu} = 62\,510\text{ cm}^{-1}$), (b) 474.7 nm ($3\bar{\nu} = 63\,204\text{ cm}^{-1}$) and (c) 469.6 nm ($3\bar{\nu} = 63\,880\text{ cm}^{-1}$) from which we deduce that in cases (a) and (b) the resonance-enhancing level should be viewed as an electronic origin, whilst in case (c) the resonance enhancement is provided by a vibrationally excited level built upon the $63\,204\text{ cm}^{-1}$ origin. The spectra are displayed with the same kinetic energy dispersion, with the scales offset so that the energies appropriate for formation of the vibrationless parent ion are aligned vertically.

energy by the electronic origin at $63\,300\text{ cm}^{-1}$ (# in Fig. 1). Similar observations have been made in recent REMPI-PES studies of other medium-sized polyatomic molecules^{20–22} and, most notably, in our own groups' study of methanethiol.⁵ The sharp photoelectron peak centred at 3.06 eV in Fig. 6 is entirely consistent with our interpretation that the $63\,300\text{ cm}^{-1}$ feature arises as a result of resonance enhancement by an electronic origin but, as already commented, we also see a number of slower peaks. As in methanethiol,⁵ we notice that the energy separations between these slower peaks and the peak at 3.06 eV match closely with the energy separations of known Rydberg origins in the $2 + 1$ REMPI spectrum and again, as previously, we interpret these observations in terms of near-resonant vibronic mixing between the $63\,300\text{ cm}^{-1}$ origin and the various manifolds of vibrational levels built on lower-lying Rydberg origins. This mixing is shown schematically in Fig. 7. Given the presumed structural similarity of the Rydberg states and the ground state ion, Franck-Condon considerations will favour preservation of the vibrational excitation upon ionisation. Hence the close similarities between the observed energy separations of the photoelectron peaks and the corresponding Rydberg origins seen in Fig. 6. However, Fig. 6 also hints at a difference between DMS and methanethiol. In the latter, presumably in part at least because of its lower (C_s) symmetry, all the identified Rydberg states were observed to provide both two- and three-photon resonance enhancements in MPI spectroscopy.⁵ Furthermore, our REMPI-PE spectra of methanethiol

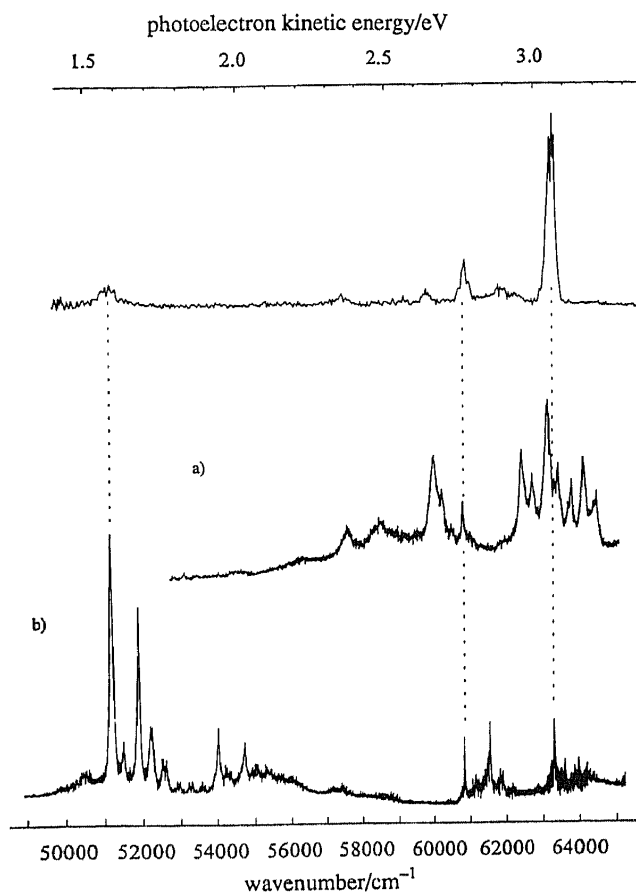


Fig. 6 REMPI-PE spectrum of DMS taken following excitation at 316.0 nm, where ionisation proceeds via a two-photon resonance ($2\tilde{\nu} = 63\,300\text{ cm}^{-1}$) involving the origin level of the first ($n = 4$) member of Series V, together with the relevant portions of the wavelength resolved 3 + 1 (a) and 2 + 1 (b) REMPI spectra of DMS, displayed on a common energy dispersion. Note how the energies of the various slower peaks in the photoelectron spectrum match closely with various of the lower lying Rydberg origins, most notably those appearing in the 2 + 1 REMPI spectrum (b).

showed slower peaks associated with all of the known lower-lying Rydberg origins (subject to the requirement that the photoelectrons had positive kinetic energy). In contrast, even a cursory examination of Fig. 1 and 2 suffices to show that the 2 + 1 and 3 + 1 REMPI spectra of the higher (C_{2v}) symmetry molecule, DMS, are largely complementary: most of the excited states that appear as two-photon resonances do not contribute to the 3 + 1 REMPI spectrum and *vice versa*. Careful inspection of the REMPI-PE spectrum shown in Fig. 6 suggests that there is a similar discrimination when it comes to deciding which Rydberg state manifolds will mix with which: slower photoelectron peaks associated with each of the Rydberg origins identified via 2 + 1 REMPI are clearly evident in the PE spectrum shown in Fig. 6, but the corresponding features associated with origins that appear as three-photon resonances are weak or, in the case of the $62\,510\text{ cm}^{-1}$ origin, absent. One plausible explanation for this observation could be that the two-photon resonances (which all fit into just two Rydberg series, see below) share the same electronic symmetry whilst some (or all) of the states providing the three-photon resonance enhancements transform differently. Further study will be needed, however, in order to validate (or refute) this speculation.

Assigning the Multiphoton Resonances

Now that we have a reasonable understanding of the vibronic character of the resonance-enhancing levels, we are in a position to offer an overall assignment of the excited electronic

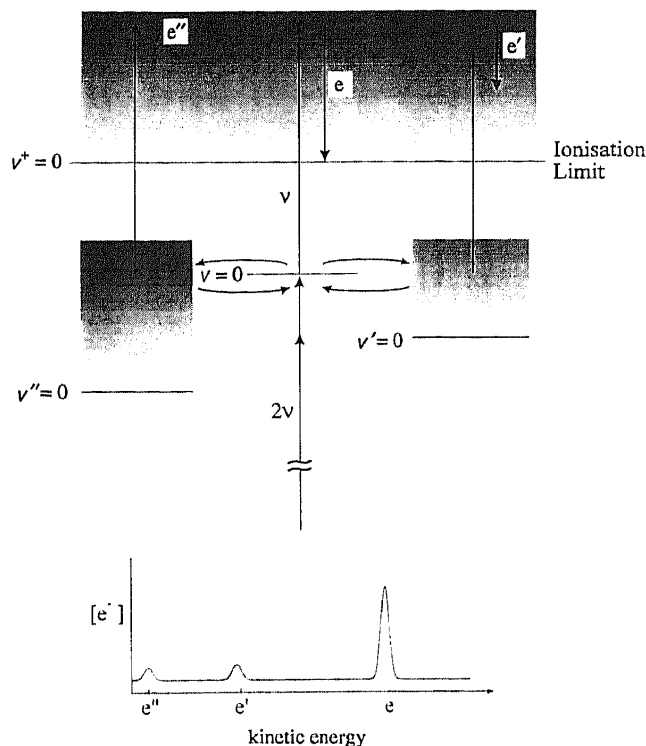
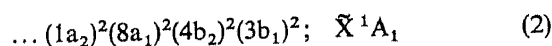


Fig. 7 Schematic illustration showing vibronic mixing between the two-photon resonant origin ($v = 0$) level of one Rydberg state and accidentally near-resonant excited vibrational levels of two lower-lying Rydberg states (whose origins are labelled $v'' = 0$ and $v' = 0$, respectively). Given that the ground state ion has an equilibrium geometry very similar to that of these various Rydberg states, the final one-photon ionisation step will tend to be Franck-Condon diagonal. Thus the vibrational quantum numbers (and the vibrational energy content) of the various interacting levels will tend to be preserved in the resulting ions and the vibronic mixing will reveal itself in the kinetic energy distribution of the accompanying photoelectrons.

states of the DMS molecule. In common with previous workers⁹⁻¹¹ we attempt to assign the observed features as members of Rydberg series converging to the first E_1 , $E_1 = 70\,250 \pm 40\text{ cm}^{-1}$. 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

$$\tilde{\nu} = E_1 - R/(n^*)^2 \quad (1)$$

where R is the Rydberg constant ($109\,737\text{ cm}^{-1}$) $n^* = (n - \delta)$ and δ is the quantum defect. For completeness, we also list the major peaks identified in the previous one-photon absorption studies.⁷⁻¹¹ The resulting quantum defects suggest assignment of four, possibly five, separate Rydberg series, including three of the series identified previously.⁹⁻¹¹ The electronic configuration of DMS in its ground state is normally written



with the highest occupied (non-bonding) $3b_1$ molecular orbital being dominated by the $3p_x$ orbital of atomic sulfur, directed perpendicular to the plane containing the C—S—C framework.¹¹ Promoting one $3b_1$ electron to higher nl Rydberg orbitals can be expected to give rise to one 's' series involving states of 1B_1 electronic symmetry with principal quantum number $n \geq 4$, 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 and one each of 1A_1 , 1A_2 and 1B_2 symmetry, all with $n \geq 3$), seven 'f'-series (two each of 1A_1 , 1A_2 and 1B_1 symmetry, the other transforming as 1B_2 , all with $n \geq 4$), etc. As in our recent work on the Rydberg states of methanethiol⁵

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

$\tilde{\nu}/\text{cm}^{-1}$	n^*	vibronic assignment	one-photon VUV ^a
series I ($n'p'b_1 \leftarrow 3b_1$)			
51 184	2.40	origin	51 165
60 854	3.42	origin	60 766
61 144		+290 cm^{-1}	
61 543		+689 cm^{-1}	
61 828		+974 cm^{-1}	
61 895		+1041 cm^{-1}	
62 172		+1318 cm^{-1}	
64 508	4.37	origin	64 547
series II ($n's'a_1 \leftarrow 3b_1$)			
	2.04		43 879
57 705	2.96	origin	57 604
58 626		+921 cm^{-1}	
63 204	3.95	origin	63 185
63 494		+290 cm^{-1}	
63 880		+676 cm^{-1}	
65 693	4.91	origin	65 645
series III			
	2.28		49 260
60 064	3.28	origin	
60 290		+226 cm^{-1}	
60 548		+484 cm^{-1}	
64 187	4.25	origin	
series IV			
62 510	3.77	origin	62 479
62 779		+269 cm^{-1}	
series V ($n'f \leftarrow 3b_1$)			
63 300	3.99	origin	
63 587		+287 cm^{-1}	
63 874		+574 cm^{-1}	
63 978		+678 cm^{-1}	
65 767	4.98	origin	
66 053		+285 cm^{-1}	
66 428		+660 cm^{-1}	
66 730		+962 cm^{-1}	
67 032		+1264 cm^{-1}	
67 091	5.96	origin	
67 362		+272 cm^{-1}	
67 887	6.92	origin	
68 482	7.97	origin	
68 826	8.90	origin	
69 078	9.97	origin	

^a Ref. 9–11.

and thiirane⁶ the parentheses are included here as a reminder that configuration interaction may 'mix' l , though not invalidate the overall state count. Analogy with atomic sulfur and with H_2S allows us to predict that 'pure' l series would exhibit quantum defects around 2.0 ('s'-series), 1.6 ('p') and 0 (for 'd', 'f' and higher l functions).^{2–4,18} Such expectations guided the assignment of one s ($\delta \approx 2.00$), one p ($\delta \approx 1.55$) and two d ($\delta \approx 0.19$ and 0.29) Rydberg series in an earlier one-photon absorption study of DMS.¹¹

The first distinctive feature in the multiphoton spectra of this molecule is an intense two-photon resonance at $51\,184\text{ cm}^{-1}$ (Fig. 1), a feature that is also clearly apparent in the previously reported one-photon VUV absorption spectra.^{9–11} Note that this resonance does not contribute to the three-photon MPI spectrum (Fig. 2) as, at the requisite photon energies, ionisation is much less probable, necessarily involving a five-photon absorption process. Previous assignments^{9–11} have suggested that this be viewed as the first ($n = 4$) member of the $np \leftarrow 3b_1$ series with a quantum defect of *ca.* 1.6. The REMPI–PE spectrum shown in Fig. 4(a)

confirms this as an origin and, given that dichroism measurements^{2,3} are consistent with the excited state having A_1 symmetry, assignment in terms of promotion to the $4p b_1$ orbital seems reasonable. However, the appearance of the $51\,184\text{ cm}^{-1}$ origin in both the one- and two-photon spectra suggests that the 'atomic' description is of limited relevance in interpreting the strength of this particular transition. The progression of smaller peaks in the region $50\,000$ – $55\,250\text{ cm}^{-1}$ are assigned in terms of vibrationally excited levels and are discussed later in this section. Here we merely note that their appearance (and the consequent implication that the geometry of this particular excited state differs from that of the ground-state neutral) might be taken as evidence that the 'Rydberg' orbital populated in this excitation probably has a significant valence contribution. Two higher-energy peaks observable in both the $2 + 1$ and $3 + 1$ spectra exhibit similar δ values and are collected together as 'series I' in Table 1.

The lowest-energy feature in the $3 + 1$ spectrum is the broad band centred around $57\,705\text{ cm}^{-1}$. A corresponding peak is also identified in the one-photon absorption study of Scott *et al.*,⁹ but it has no obvious counterpart in the two-photon spectrum. Measurement of the kinetic energies of the photoelectrons resulting from $3 + 1$ REMPI at this wavelength (519.9 nm) confirms that this feature is an electronic origin. Both this, and the near-integer quantum defect, suggest that this should be assigned in terms of excitation to a Rydberg orbital with predominant s or d character. This feature has been previously assigned as the second ($n = 5$) member of the $n's'a_1 \leftarrow 3b_1$ series, the first member of which is observed in one-photon absorption centred at *ca.* 228 nm .^{9,10,23} Higher-energy members of this series (labelled 'series II' in Table 1) are seen in one photon absorption^{9–11} and are clearly evident as three-photon resonances in Fig. 2.

The remaining structure evident in the $3 + 1$ REMPI spectrum (Fig. 2) presents more of a puzzle; indeed, prior to our obtaining the associated REMPI–PE spectra it appeared quite unintelligible. The REMPI–PES studies show that three of the $3 + 1$ MPI resonances at energies $> 60\,000\text{ cm}^{-1}$ correspond to further, hitherto unassigned, electronic origins. Two of these, centred at $60\,064\text{ cm}^{-1}$ and $64\,187\text{ cm}^{-1}$, respectively, show similar quantum defects and are grouped together as 'series III' in Table 1; neither has any counterpart in the $2 + 1$ REMPI spectrum, nor have they been recognised in any of the previous one-photon absorption studies.^{9–11} We note, however, that the broad, intense one-photon resonance centred at *ca.* 203 nm has a quantum defect appropriate for it being the first member of this series. The assignment of these features remains problematic: quantum defect considerations would tend to suggest the orbital promotion $np \leftarrow 3b_1$, but such an assignment would run counter to the $\Delta l = \text{odd}$ change in the orbital angular momentum quantum number implied by their observation as three, but not two, photon resonances. The $62\,510\text{ cm}^{-1}$ feature is also found to be an electronic origin. It, too, has no analogue in either the one- or two-photon excitation spectrum. Its quantum defect would be consistent with the orbital promotion $3d \leftarrow 3b_1$, but we have not identified any higher energy resonances that would serve to extend this 'series IV'.

We now return to the $2 + 1$ REMPI spectrum of DMS (Fig. 1) and, in particular, the well developed series of sharp features ('series V') beginning at $63\,300\text{ cm}^{-1}$. These resonances are not evident in the $3 + 1$ REMPI spectrum, nor in any of the previous one-photon absorption spectra.^{9–11} Their quantum defects (*ca.* 0 assuming that the $63\,300\text{ cm}^{-1}$ member has $n = 4$) are fully consistent with the assignment $nf \leftarrow 3b_1$ (*i.e.* a $\Delta l = +2$ transition in the atomic limit). Such an observation should come as no surprise: similar series

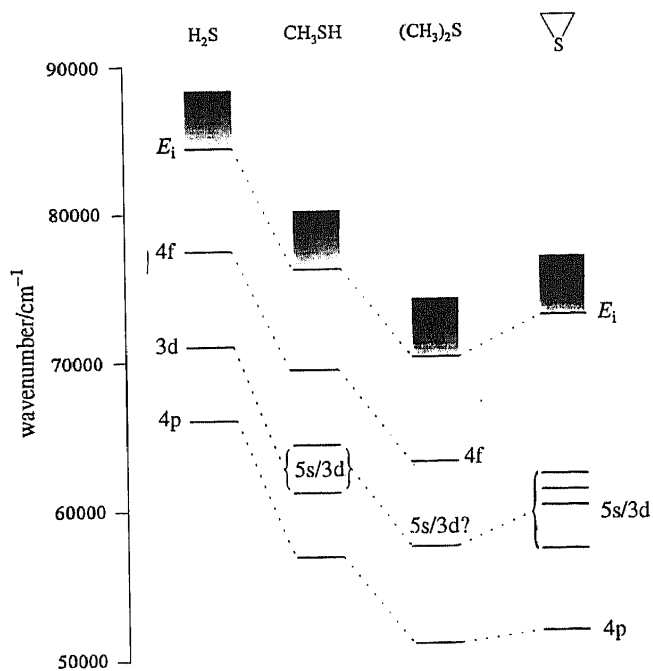


Fig. 8 Plot illustrating the very similar term values (with respect to ionisation) of some of the more prominent Rydberg states of hydrogen sulfide,²⁻⁴ methanethiol,⁵ dimethyl sulfide and thiirane⁶

have been identified in recent multiphoton studies of H₂S⁴ and methanethiol.⁵ Recall that Fig. 6 showed the photoelectron kinetic energy spectrum following 2 + 1 REMPI via the 63 300 cm⁻¹ feature and revealed substantial vibronic mixing with near-resonant vibrationally excited levels of two lower-energy origins, both assigned as members of the n'p'b₁ ← 3b₁ series. In the light of our earlier speculation it is tempting to suggest that the series V members have the same ¹A₁ electronic symmetry. Fig. 8 serves to parallel the similarities in the term values observed for the lower members of the prominent Rydberg series identified in H₂S, CH₃SH, DMS and thiirane. Finally, we comment that we have not been able

Table 2 Observed vibronic structure associated with the 4'p'b₁ ← 3b₁ Rydberg transition in DMS

ν/cm^{-1}	$\Delta\nu/\text{cm}^{-1}$	assignment
50 473	- 711	6 ₁ ⁰
51 184 (51 192)	0	0 ₀ ⁰
51 474 (51 485)	+ 291	7 ₁ ⁰
51 883 (51 894)	+ 699	6 ₀ ¹
52 207 (52 235)	+ 1023	5 ₀ ¹
52 498 (52 510)	+ 1314	4 ₀ ¹
52 577 (52 589)	+ 1393	6 ₀ ²
52 871 (52 890)	+ 1687	6 ₀ ² 7 ₀ ⁰
52 932 (52 939)	+ 1748	5 ₀ ¹ 6 ₀ ¹
53 194 (53 200)	+ 2010	4 ₀ ¹ 6 ₀ ¹
53 284 (53 237)	+ 2100	5 ₀ ¹ 6 ₀ ¹ 7 ₀ ¹
53 581 (53 558)	+ 2397	4 ₀ ¹ 5 ₀ ¹
54 018 (53 978)	+ 2834	2 ₀ ¹
54 236 (54 244)	+ 3052	4 ₀ ¹ 5 ₀ ¹ 6 ₀ ¹
54 312	+ 3128	2 ₀ ¹ 7 ₀ ¹
54 714	+ 3530	2 ₀ ¹ 6 ₀ ¹
55 024	+ 3840	2 ₀ ¹ 5 ₀ ¹
55 240	+ 4056	2 ₀ ¹ 4 ₀ ¹

Values in brackets show estimates of the corresponding band maxima as seen in the room-temperature absorption spectrum (ref. 10)

to identify any features in the REMPI spectrum of DMS that might be associated with the additional weak series (labelled d', and with $\delta \approx 0.29$) tentatively identified in absorption by Tokue *et al.*¹¹ (though not in any other one-photon absorption study.^{9,10})

Excited-state and Ion Vibrational Frequencies

Allkins and Hendra¹⁹ have discussed the 21 fundamental vibrations of DMS, including the seven totally symmetric (a₁) modes. Most, if not all, of these a₁ vibrations appear as short

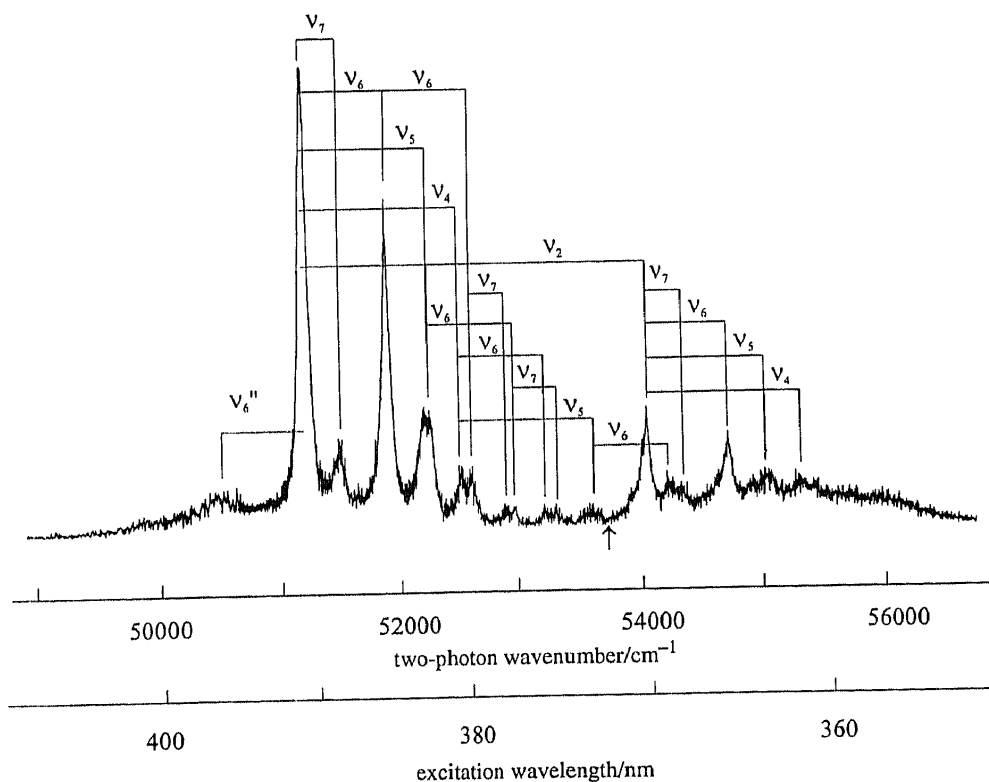


Fig. 9 Expanded view of the 2 + 1 REMPI spectrum of DMS in the region of the first (n = 4) member of the n'p'b₁ ← 3b₁ Rydberg series (series I in Table 1), indicating the vibrational progressions built upon this electronic origin

Table 3 Frequencies (in cm^{-1}) of the various a_1 vibrational modes of the ground state of the DMS cation

assignment	description	ground-state ion frequencies / cm^{-1}	ground-state frequencies / cm^{-1}
ν_1	C—H stretch		2980
ν_2	C—H stretch	2840	2935
ν_3	CH_3 deformation		1434
ν_4	CH_3 deformation	1300	1327
ν_5	CH_3 rock	1040	1022
ν_6	C—S stretch	700	684
ν_7	C—S—C deformation	280	284

Values for the frequencies of the corresponding modes in the ground-state neutral (ref. 19) are included for comparison.

progressions in at least some of the Rydberg transitions observed both in the present multiphoton work and in the previous one-photon absorption studies.^{9–11} The expanded wavelength scan shown in Fig. 9 shows them to be especially evident in the first ($n = 4$) members of series I. Table 2 includes a listing of the wavenumbers of the observed band centres associated with this particular Rydberg transition, together with proposed vibronic assignments. Note that, notwithstanding our earlier speculations concerning possible valence dilution of this Rydberg transition, the excited-state vibrational frequencies implied by our assignments are generally close to the corresponding ground-state values and that, because of their near degeneracies, we are unable to say whether the *ca.* 1300 cm^{-1} interval reflects activity in ν_3 and/or ν_4 and, similarly, whether the *ca.* 2840 cm^{-1} interval should be associated with one or other or both of the C—H stretching modes ν_1 and ν_2 . As we have already seen (*e.g.* Fig. 4) the PE spectra obtained following REMPI *via* such well resolved vibronic features as these are particularly clean and unambiguous (reflecting the very similar geometries of the Rydberg states and the ground-state ion) and provide a ready route to estimating the wavenumbers of the corresponding a_1 vibrational modes in the ground state of the ion. Table 3 presents a comparison of the values so derived with those of their counterparts in the neutral molecule.

Conclusion

This multiphoton investigation of the Rydberg states of DMS provides yet another illustration of the way in which REMPI spectroscopy, especially when coupled with REMPI-PES, can supplement conclusions drawn from conventional one-photon VUV absorption spectroscopy. The present work confirms, and slightly refines, literature values for the first adiabatic E_i of DMS, $E_i = 8.710 \pm 0.005 \text{ eV}$, and allows identification of members of at least four Rydberg series, three of which have been observed in the previous one-photon studies.^{9–11} The fourth, previously unobserved, series we associate with promotion of an electron from the highest occupied ($3b_1$) molecular orbital of the ground-state configuration to Rydberg orbitals with predominantly f ($l = 3$) character. Finally, careful inspection of the REMPI-PE spectra

reveals the presence of one or more peaks indicative of slower photoelectrons which, as in methanethiol,⁵ we suggest provides evidence of vibronic mixing between the manifolds of vibrational levels associated with the various Rydberg states.

The Bristol group is grateful to the EPSRC (formerly SERC) for equipment grants and for a studentship to R.A.M., and to Mr K. N. Rosser for his advice and encouragement. A.J.O.-E. thanks the Royal Society for the award of his Eliz. Challenor Research Fellowship, whilst M.N.R.A. is grateful to the Ciba Fellowship Trust for their support of the Bristol–Amsterdam collaboration. The Amsterdam group is grateful to the Netherlands Organisation for Scientific Research (NWO) for equipment grants and financial support.

References

- 1 S. B. Barone, A. A. Turnipseed and A. R. Ravishankara, *Faraday Discuss.*, 1995, **100**, and references therein, in the press.
- 2 M. N. R. Ashfold, J. M. Bayley, R. N. Dixon and J. D. Prince, *Chem. Phys.*, 1985, **98**, 289.
- 3 C. A. Mayhew, J.-P. Connerade, M. A. Baig, M. N. R. Ashfold, J. M. Bayley, R. N. Dixon and J. D. Prince, *J. Chem. Soc., Faraday* **2**, 1987, **83**, 417.
- 4 M. N. R. Ashfold, W. S. Hartree, A. V. Salvato, B. Tutchter and A. Walker, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 2027.
- 5 R. A. Morgan, P. Puyuelo, J. D. Howe, M. N. R. Ashfold, W. J. Buma, N. P. L. Wales and C. A. de Lange, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 2715.
- 6 R. A. Morgan, P. Puyuelo, J. D. Howe, M. N. R. Ashfold, W. J. Buma, J. B. Milan and C. A. de Lange, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 3591.
- 7 W. C. Price, J. P. Teegan and A. D. Walsh, *Proc. R. Soc. A.*, 1950, **201**, 600.
- 8 L. B. Clark and W. T. Simpson, *J. Chem. Phys.*, 1965, **43**, 3666.
- 9 J. D. Scott, G. C. Causley and B. R. Russell, *J. Chem. Phys.*, 1973, **59**, 6577.
- 10 R. McDiarmid, *J. Chem. Phys.*, 1974, **61**, 274.
- 11 I. Tokue, A. Hiraya and K. Shobatake, *Chem. Phys.*, 1989, **130**, 401.
- 12 M. B. Robin, *Higher Excited States of Polyatomic Molecules*, Academic Press, New York, 1974, vol. 1; 1985, vol. 3.
- 13 V. Galasso, *J. Phys. B.*, 1989, **22**, 2241.
- 14 K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki and S. Iwata, *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules*, Japan Scientific Societies Press, Tokyo, 1981.
- 15 M. N. R. Ashfold, A. D. Couch, R. N. Dixon and B. Tutchter, *J. Phys. Chem.*, 1988, **92**, 5327.
- 16 B. G. Koenders, D. M. Wieringa, K. E. Drabe and C. A. de Lange, *Chem. Phys.*, 1987, **118**, 113.
- 17 N. P. L. Wales, E. de Beer, N. P. C. Westwood, W. J. Buma, C. A. de Lange and M. C. van Hemert, *J. Chem. Phys.*, 1994, **100**, 7984.
- 18 W. C. Martin, R. Zalubas and A. Musgrove, *J. Phys. Chem. Ref. Data*, 1990, **19**, 821.
- 19 J. R. Allkins and P. J. Hendra, *Spectrochim. Acta*, 1966, **22**, 2075.
- 20 M. R. Dobber, W. J. Buma and C. A. de Lange, *J. Chem. Phys.*, 1993, **99**, 836.
- 21 P. M. Weber and N. Thantu, *Chem. Phys. Lett.*, 1992, **197**, 556.
- 22 S. Hillenbrandt, L. Zhu and P. Johnson, *J. Chem. Phys.*, 1989, **92**, 870.
- 23 D. D. Altenloh and B. R. Russell, *Chem. Phys. Lett.*, 1981, **77**, 217.