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Observation of the SCl Radical by Resonance-enhanced Multiphoton Ionisation Spectroscopy

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We report the first observation of any excited electronic state of the SCl radical. SCl ($X^2\Pi$) radicals are produced by photolysis of SCl_2 vapour at near-UV wavelengths around 343 nm, and detected by multiphoton ionisation spectroscopy, resonance enhanced at the two-photon energy by a Rydberg state of $^2\Pi$ electronic symmetry. We suggest that this state derives from an electronic configuration involving a $4p\pi$ Rydberg electron built on the $^3\Sigma^-$ ground-state ion core. Analysis of the (partially) rotationally resolved resonance-enhanced multiphoton ionisation (REMPI) spectra seems most fully consistent with all transitions originating exclusively from $X^2\Pi_{3/2}$ levels of both the $^{32}\text{S}^{35}\text{Cl}$ and $^{32}\text{S}^{37}\text{Cl}$ isotopomers and yields the term value for the newly identified $^2\Pi$ state ($\nu_0 = 58\,220 \pm 20 \text{ cm}^{-1}$) measured relative to the lower ($X^2\Pi_{3/2}$) spin-orbit component of the ground state. The excited state is shown to have a bond length *ca.* 13% shorter than that of the ground-state neutral. Parallel REMPI-photoelectron spectroscopy (PES) studies yield values of $9.57 \pm 0.01 \text{ eV}$ for the first ionisation energy (E_i) of SCl (measured relative to the lower, $^2\Pi_{3/2}$, spin-orbit component of the ground state), and $685 \pm 30 \text{ cm}^{-1}$ for the vibrational level separation in the ground-state ion (*ca.* 19% higher than that of the corresponding energy interval in the ground-state neutral).

REMPI spectroscopy is making an ever greater contribution to our knowledge and understanding both of the structure and the stability of higher excited electronic states (most notably Rydberg states) of molecules,^{1–3} including free-radical species.^{4,5} This contribution describes use of the REMPI technique to provide the first observation of any excited electronic state of the SCl free radical. The literature contains little detailed spectroscopic information about this radical. The first reported observation of SCl radicals was in an Ne matrix, following 248 nm photolysis of SCl_2 and S_2Cl_2 .⁶ Somewhat unusually, there does not appear to be any microwave data pertaining to this radical. However, IR diode laser experiments, in which gas-phase SCl radicals were produced either by passing a dc discharge through a flowing S_2Cl_2 (or SCl_2)– H_2 –He mixture⁷ or by 248 nm photodissociation of SCl_2 and S_2Cl_2 ⁸ have provided spectroscopic constants for the lower ($^2\Pi_{3/2}$) spin-orbit component of the $\nu'' = 0$ and 1 levels of both the $^{32}\text{S}^{35}\text{Cl}$ and $^{32}\text{S}^{37}\text{Cl}$ isotopomers. The fundamental vibrational interval in the $X^2\Pi_{3/2}$ state of $^{32}\text{S}^{35}\text{Cl}$ was thereby determined to be 574.61 cm^{-1} . One additional absorption band identified in the latter study⁸ was tentatively assigned as the $^2\Pi_{3/2}$ ($\nu = 2 \leftarrow \nu = 1$) hot-band transition. Such an interpretation means that the upper ($^2\Pi_{1/2}$) spin-orbit component of the ground state remains unobserved. Analogy with SF, combined with knowledge of the spin-orbit coupling constants for S and Cl, suggests a value of *ca.* -400 cm^{-1} for the ground-state spin-orbit splitting in SCl.⁷ SCl radicals have also been detected mass spectrometrically following 308 nm photodissociation of S_2Cl_2 ; these are believed to arise *via* secondary photolysis of the primary S_2Cl radicals.⁹

The ground-state electronic configuration of the SCl radical can be written

No experimental information relating to the SCl^+ ion is available currently in the literature but, by analogy with the S_2 radical, which is isoelectronic with SCl^+ , the ground state can be expected to arise as a result of removal of a 4π electron to yield an ion of $^3\Sigma^-$ symmetry.

Here we report the observation of two partially resolved REMPI spectra of highly rotationally excited SCl(X) photo-fragments resulting from near-UV photolysis of SCl_2 . Rotational analysis shows these bands to be associated with two-photon resonances involving an excited (Rydberg) state of $^2\Pi$ symmetry. The observed blue degradation of the bands is wholly consistent with our assumption that the excitation involves electron promotion from the anti-bonding 4π orbital. However, a more detailed assignment of the vibrational states and/or the spin-orbit components responsible for the observed REMPI spectra presents some ambiguities. Consistent with previous studies^{7,8} our favoured analysis assumes that the spectra are carried by SCl ($X^2\Pi_{3/2}$) photo-fragments in their $\nu'' = 0$ and 1 vibrational levels. Companion studies of the kinetic energies of the photoelectrons resulting from REMPI *via* the newly identified $^2\Pi$ excited state provide a value of $9.57 \pm 0.01 \text{ eV}$ (measured relative to the lower $^2\Pi_{3/2}$ component of the ground-state neutral) for the first ionisation energy of the SCl radical. Quantum defect considerations lead us to suggest that the configuration $\cdots (9\sigma)^2(3\pi)^4(4\pi)^2[{}^3\Sigma^-](4p\pi)^1$ makes the dominant contribution to the electronic wavefunction of the newly identified excited $^2\Pi$ state.

Experimental

The apparatus and the operating procedures involved in the respective experiments in Bristol and Amsterdam used to obtain the present results have been fully described in previous publications^{10–14} and are not repeated here. In both experiments SCl(X) radicals were produced by photolysis of SCl_2 .

Mass-resolved REMPI spectra of SCl radicals were obtained in Bristol by expanding pure SCl_2 vapour (Aldrich, vapour pressure *ca.* 100 Torr) through a pulsed nozzle into the source region of a home-built time-of-flight (TOF) mass spectrometer^{10,11} and using an excimer pumped dye laser operating with the dye *p*-terphenyl both to photolyse the SCl_2 precursor and to effect REMPI of the resulting SCl(X) fragments. Comparatively soft focusing (30 cm focal length

lens) and laser energies $< 1 \text{ mJ pulse}^{-1}$ were used, in order to minimise the large non-resonant background ion signals in the S^+ and SCl^+ mass channels observed at higher light intensities. The origin of these background signals is presumed to be non-resonant ionisation of SCl_2 , followed by fragmentation of the ion to yield ionic fragments. Calibration of the wavelength resolved REMPI spectra was achieved *via* simultaneous monitoring of atomic Ne transitions excited in a hollow cathode lamp.

Complementary REMPI-PES data pertaining to the SCl radical were recorded in Amsterdam by leaking SCl_2 vapour through a capillary into the interaction region of a 'magnetic bottle' spectrometer^{12,13} and, as in Bristol, both photolysing this precursor and ionising the resulting SCl(X) fragments with the output of a single excimer pumped dye laser. The measured photoelectron kinetic energies were put on an absolute scale by simultaneous measurement of the kinetic energies of electrons resulting from the direct one-photon ionisation of electronically excited sulfur atoms produced in the photoexcitation process.

Results

Wavelength-resolved REMPI

Fig. 1 and 2 show spectra obtained using linearly polarised photoexcitation in the wavelength range 346.5–340 nm, recorded with the Bristol apparatus using mass-resolved ion detection. Two bands are discernible for each isotopomer; henceforth we shall refer to these as bands A (Fig. 1) and B (Fig. 2). These spectra are not corrected for wavelength-dependent variations in the dye laser output energy. This most notably affects the appearance of the low-wavenumber end of band B which is underestimated in Fig. 2. We searched the entire wavelength region 370–310 nm, but no additional

resonances attributable to the SCl radical were observed. We are confident in assigning bands A and B to transitions involving the SCl radical for the following reasons: (i) The times of flight of the ions responsible for the spectra are consistent with m/z ratios of 67($^{32}\text{S}^{35}\text{Cl}$) and 69($^{32}\text{S}^{37}\text{Cl}$), respectively. (ii) The relative intensities of the two isotopic variants of both band A and band B are consistent with the expected isotope abundance ratio $^{32}\text{S}^{35}\text{Cl} : ^{32}\text{S}^{37}\text{Cl} \approx 3 : 1$. (iii) Given the paucity of peaks in the ion TOF spectrum it is worth considering whether the mass calibration could be sufficiently in error that a species such as S_2 (m/z 64) or Cl_2 (m/z 70, 72 and 74) was actually responsible for these spectra. Both of these spectral carriers can be discounted on the grounds that the TOF spectrum associated with the S_2 radical should show just one strong isotope, whilst Cl_2 should show three isotopomers, two of which would display intensity alternations in the rotational structure due to the influence of nuclear spin statistics.

Several points emerge from a careful examination of Fig. 1 and 2. Though none of the bands appear particularly strongly in the present work, the shorter-wavelength features (band A) are clearly the more intense. Each band shows no discernible band head, is blue degraded and appears to be composed of two branches which come in and out of 'phase' as the wavelength is scanned. This is illustrated in Fig. 3, which shows an expanded view of part of band A for the $^{32}\text{S}^{35}\text{Cl}$ isotopomer.

The parent SCl_2 molecule shows a continuous absorption at these near UV wavelengths.¹⁵ On energetic grounds and by analogy with previous photodissociation studies of SCl_2 it is reasonable to suppose that we are observing SCl molecules in their ground ($X^2\Pi$) electronic state and our initial analyses build on this assumption (which we substantiate below).

The lower $^2\Pi_{3/2}$ spin-orbit component has been characterised by IR diode laser experiments and rotational constants

Fig. 1 Two-photon REMPI spectrum of the $^{32}\text{S}^{35}\text{Cl}$ (lower trace) and $^{32}\text{S}^{37}\text{Cl}$ (upper trace) isotopomers recorded using linearly polarised laser radiation in the wavelength range 343.2–340.2 nm (described herein as band A)

Fig. 2 Two-photon REMPI spectrum of the $^{32}\text{S}^{35}\text{Cl}$ (lower trace) and $^{32}\text{S}^{37}\text{Cl}$ (upper trace) isotopomers recorded using linearly polarised laser radiation in the wavelength range 346.5–343.8 nm (described herein as band B)

are available.^{7,8} Unfortunately, with just two (often blended) branches per band and a rather large laser linewidth relative to the rotational constant we were not able to obtain unambiguous ground-state combination differences in these spectra. Further insight into the nature of these transitions requires knowledge of the associated REMPI-PE spectra.

REMPI-PE

Fig. 4 shows a typical REMPI-PE spectrum, recorded in Amsterdam with the laser wavelength tuned to a sharp feature in band A ($2\tilde{\nu} = 58\,359.2\text{ cm}^{-1}$). Five photoelectron peaks are clearly discernible. By recording wavelength-

Fig. 3 Expanded view of band A of the $^{32}\text{S}^{35}\text{Cl}$ isotopomer in the wavelength range 343.2–341.5 nm. The combs superimposed over the spectrum indicate the way in which the individual $^{\text{Q}}\text{Q}$ and $^{\text{R}}\text{Q}$ branch transitions run in and out of phase with increasing J . Rotational analysis of lines beneath the bold comb is presented in the text.

Fig. 4 REMPI-PES obtained following laser excitation of SCl_2 at $29\,179.6\text{ cm}^{-1}$. Peaks II and III are identified with photoelectrons arising from three-photon ionisation of SCl(X) radicals. The other peaks are assigned to non-resonant one-photon ionisation of sulfur atoms formed in the following excited states: $[\text{S}^*]4p, {}^3\text{P}$ (peak I); $[\text{S}^*]4p, {}^3\text{P}$ (peak IV); $[\text{S}^*]3d, {}^3\text{D}^\circ$ and $[\text{S}^*]4s, {}^3\text{D}^\circ$ (blended in peak V).

resolved excitation spectra whilst monitoring each of these photoelectron peaks individually it was possible to determine that only the peaks labelled II and III in Fig. 4 correlated with the (sum of the two) spectra shown in Fig. 1, thereby identifying these two peaks as being associated with photoelectrons arising from the ionisation of SCl radicals. The other four peaks (labelled I, IV and V) can all be assigned in terms of non-resonant, one-photon ionisation of electronically excited sulfur atoms. The atomic assignments, detailed in the caption to Fig. 4, are unambiguous; the energy spacings of the relevant photoelectron peaks are in complete accord with the separations between the documented energy levels of atomic sulfur.¹⁶ Given that the ionisation energy of atomic sulfur is known precisely ($83\,559.3\text{ cm}^{-1}$), these peaks provide a very convenient internal calibration of the measured photoelectron kinetic energies. We presume that these highly excited sulfur atoms (carrying electronic excitation in excess of $60\,000\text{ cm}^{-1}$) arise as a result of higher-order multi-photon absorption processes in the SCl_2 precursor.

The simplicity of that portion of the REMPI-PE spectrum which we attribute to the SCl radical (only peaks II and III in Fig. 4) suggests that the $\text{SCl}^+ \leftarrow \text{SCl}^*$ ionisation step is strongly Franck-Condon diagonal, *i.e.* involves a $\Delta v = 0$ transition. If, for the moment, we assume that our band A is an electronic origin transition (this we justify below) then the photoelectron peak observed at 1.263 eV (peak III in Fig. 4) represents ionisation to a vibrationless level of SCl^+ . We abbreviate such an excitation scheme as $(0 \leftarrow 0 \leftarrow 0)$, implying $\text{SCl}_{v=0}^+ \leftarrow \text{SCl}_{v=0}^* \leftarrow \text{SCl(X)}_{v=0}$. If we further assume that the ionisation process yields SCl^+ molecules in their ground electronic state, then the present measurement of the kinetic energy of these photoelectrons establishes an effective ionisation energy (E_i) of SCl as $9.59 \pm 0.01\text{ eV}$. This value of the E_i presumes an ionisation process involving a total of three photons. Alternative values derived assuming that ionisation involves a total of either two or four photons are not consis-

tent with physical intuition. At this stage, it should be remembered that this effective ionisation energy is derived by studying the ionisation of SCl molecules with $J \neq 0$. An estimation of the energy correction needed to yield the E_i for the non-rotating molecule is presented later.

REMPI-PE spectra recorded with the excitation laser tuned to resolved features within band B show a very similar appearance but with all peaks shifted to lower kinetic energy by an amount consistent with the decrease in photon energy. In all REMPI-PE spectra exhibiting an intense peak III we also observe a small additional peak displaced to lower kinetic energies by $0.085 \pm 0.004\text{ eV}$, *e.g.* peak II in Fig. 4. Wavelength scans confirm that this photoelectron peak is also associated with the SCl radical; we assign it in terms of ionisation yielding SCl^+ ions in their $v = 1$ level, *i.e.* a $(1 \leftarrow 0 \leftarrow 0)$ ionisation scheme. Thus we derive a value (averaged over several spectra) of $685 \pm 30\text{ cm}^{-1}$ for the energy separation between the $v = 1$ and $v = 0$ levels in the ground state of the SCl^+ ion, a value some 19% larger than that of the corresponding level spacing in the ground-state neutral.⁸

Discussion

Here we bring together all of the clues gleaned from the ion- and photoelectron-detected data outlined above in order to try and gain further insight into the nature of the state(s) which give rise to the wavelength-resolved spectra presented earlier. As already stated, the deduced propensity for a $\Delta v = 0$ transition in the $\text{SCl}^+ \leftarrow \text{SCl}^*$ ionisation step implies that the resonance-enhancing state (SCl^*) has a bond length similar to that of the ground-state ion. This is most simply rationalised by assuming the excited state to be a member of a Rydberg series converging to the ground state of the ion. As stated earlier, it seems logical that these transitions are from the ground-state $X\text{ }^2\Pi$ to the Rydberg state and thus the observed ionisation is the result of a $2 + 1$ REMPI process.

Given that the ground state has $^2\Pi$ symmetry, fully allowed two-photon excitations could result in population of excited states of $^2\Sigma$, $^2\Pi$, $^2\Delta$ or $^2\Phi$ electronic symmetry. However, trial simulations of the likely form of the rotational fine structure associated with each of these possible two-photon excitations quickly reveal that such spectral simplicity is only compatible with a $^2\Pi \leftarrow ^2\Pi$ two-photon transition, carried by the $T_0^0(A)$ zero-rank component of the two-photon transition operator. If, as suggested earlier, this excited $^2\Pi$ state is a member of a Rydberg series converging to the $^3\Sigma^-$ ground state of the ion then the orbital degeneracy is localised not in the core, but in the diffuse Rydberg electron, and we can anticipate minimal (though, in principle, resolvable) spin-orbit splitting. As Fig. 5 shows, a $^2\Pi$ [case(b)] $\rightarrow$ $^2\Pi$ [case(a)] two-photon transition, carried by the $T_0^0(A)$ zero-rank component of the two-photon transition operator, should consist of two bands separated by the ground-state spin-orbit splitting. Each band will consist of just two rotational branches, and while this detail accords with the experimental observation (Fig. 1-3), it is in fact premature to conclude that this spin-orbit splitting is the explanation for the separation of bands A and B.

It is possible to make an estimate of the J assignments, and of the change in rotational constant involved in the $\text{SCl}^* \leftarrow \text{SCl(X)}$ two-photon transition, by modelling the variation in the spacings between successive lines of the $^2\Pi$ branch. In the rigid-rotor limit, the rotational contribution to the term values of the upper and lower $^2\Pi$ states may be approximated as:

$$F'(N) = B'[N'(N' + 1) - \Lambda'^2]; \text{ assuming } A' \text{ and } \gamma' = 0 \quad (2)$$

$$F''(J) = B''[J''(J'' + 1) - \Omega''^2]; \text{ where } J = N \pm \frac{1}{2} \quad (3)$$

Fig. 5 Schematic energy-level diagram illustrating the rotational branches that accompany a two-photon ${}^2\Pi$ [case (b)]- ${}^2\Pi$ [case (a)] transition carried by the $T_0^0(A)$ scalar component of the two-photon transition operator

As Fig. 5 shows, ${}^QQ$ two-photon transitions originating from the $X\,{}^2\Pi_{3/2}$ state terminate on F_1 levels in the upper ${}^2\Pi$ state. For such F_1 levels, $J = N + \frac{1}{2}$ and $N = J - \frac{1}{2}$. Thus the wavenumber separation of the various ${}^QQ$ transitions will be given by an expression of the form

$${}^QQ(J) = \tilde{\nu}_0 + B'[(J - \frac{1}{2})(J + \frac{1}{2}) - A'^2] - B''[J(J + 1) - \Omega'^2] \quad (4)$$

and the difference between adjacent ${}^QQ$ lines by

$$\Delta[{}^QQ(J)] = 2\Delta B(J + \frac{1}{2}) - B'' \quad (5)$$

where $\Delta B = B' - B''$.

Fig. 6 shows a plot of the measured differences, $\Delta[{}^QQ(J)]$, between consecutive lines in one of the two identified progressions in band A of $S^{35}\text{Cl}$ (those indicated by the bolder of the two combs in Fig. 3) against $(J + \frac{1}{2})$, together with the best-fit straight line. In constructing this plot, the J assignments were varied so as to give an intercept as close as possible to the known value of $-B''$ as required by eqn. (5). In the rigid-rotor limit the gradient of this plot is simply $2\Delta B$. Thus we obtain $\Delta B = +0.035 \pm 0.003\text{ cm}^{-1}$, where the quoted uncertainty is the error (3σ) of the fit. This result implies that $B' = 0.293 \pm 0.003\text{ cm}^{-1}$. Similar analysis of the other progression identified in band A (indicated by the fainter comb in Fig. 3) yields a very similar value (to within 1σ) for ΔB . This fitting procedure also allows estimation of the absolute J quantum numbering in the rotational branches, *e.g.* the analysis implies that the longest-wavelength ${}^QQ$ lines included in this analysis of $S^{35}\text{Cl}$ band A involve levels with $J'' \approx 50.5$. This, in turn, predicts the origin of this ${}^2\Pi$ - ${}^2\Pi_{3/2}$ sub-band to be at $58\,220 \pm 20\text{ cm}^{-1}$. The large error quoted here reflects the fact that our analysis incorporates a rigid-rotor approximation and has neglected any contributions from spin-orbit and/or spin-rotation interactions in the upper state; inclusion of non-zero values for D' , A' and/or γ' would almost certainly modify our proposed J assignment and thus our value for ν_0 .

Fig. 6 Measured wavenumber separations, $\Delta[{}^QQ(J)]$, between consecutive lines in one of the rotational progressions in band A (the one indicated by the bolder comb in Fig. 3) vs. $(J + \frac{1}{2})$, together with the best-fit straight line (corresponding to $y = 0.070x - 0.2551$). In constructing this plot, the J assignments were varied so as to give an intercept on the vertical axis that best matched the known value of $-B''$, as required by eqn. (5).

These spectroscopic parameters enable qualitative, though not quantitative, replication of the experimental REMPI spectra. Fig. 7 shows several simulations of the scalar part of a ${}^2\Pi$ - ${}^2\Pi_{3/2}$ two-photon transition using $B' = 0.293\text{ cm}^{-1}$, literature⁷ values for B'' (0.257907 cm^{-1}) and D'' ($2.29 \times 10^{-7}\text{ cm}^{-1}$) and assuming a Boltzmann rotational-state population distribution characterised by $T_{\text{rot}} = 1000\text{ K}$. These highlight the extreme sensitivity of the interference between the ${}^QQ$ and ${}^RQ$ branches (as observed experimentally) to small changes in the value assumed for the upper-state centrifugal distortion constant; similar effects can be achieved by subtle variations in the assumed value of A' and/or γ' . Extensive trial simulations failed to reproduce the exact pattern of the experimental spectrum, but this is not surprising given the quality of the experimental data and the number of parameters that could be included in the simulations. If we concentrate further on comparison of the simulated contours with band A, across which the dye laser intensity was most nearly constant, one unambiguous conclusion does emerge; the rotational-state population distribution of our SCl radicals appears decidedly non-Boltzmann. For example, we are unable to discern any low- J lines in the experimental spectra. This might indicate some marked rotational level dependence to our REMPI detection efficiency, but this seems unlikely. Further simulations¹⁷ reveal that the general form of the experimental spectra is replicated much better if we assume a symmetrical (*e.g.* Gaussian) population distribution over the J'' states, peaking at $J'' \approx 85.5$ and with a width $\Delta J'' \approx 30$ (FWHM). The likely source of such a distribution is discussed later.

We now return to the identity of the states responsible for the bands A and B in the REMPI spectrum. Fig. 8 outlines schematically three possible excitation schemes all of which could be compatible with the experimental observations as presented to date. Fig. 8(a) and (b) both assume that band A involves a two-photon resonance linking the $X\,{}^2\Pi_{3/2}$ spin-orbit component and the $\nu' = 0$ level of the newly identified ${}^2\Pi$ state. They differ only in the assignment of the lower level involved in band B. In Fig. 8(a) we assume that level to be the $\Omega = 1/2$ component of the ground vibronic level whereas in (b) we take this level to be the $\Omega = 3/2$ component of $\nu'' = 1$. The alternative scheme [Fig. 8(c)] proposes that both bands A and B originate from a common lower level and that the observed separation is a property of the resonant-enhancing state of the neutral.

Fig. 7 (a) Simulated stick spectra of the scalar part of a $^2\Pi-^2\Pi_{3/2}$ two-photon transition assuming the following parameters: ground-state rotational constants, $B'' = 0.257907 \text{ cm}^{-1}$ and $D'' = 2.29 \times 10^{-7} \text{ cm}^{-1}$ (both from ref. 7), a band origin, $\nu_0 = 0$, excited-state rotational constants, $B' = 0.293 \text{ cm}^{-1}$ and $D' = 0$, and a Boltzmann rotational-state population distribution characterised by $T_{\text{rot}} = 1000 \text{ K}$. Simulations (b)–(d), each of which are plotted assuming a Gaussian lineshape of 0.6 cm^{-1} (FWHM), illustrate the extreme sensitivity of the interference between the $^{\text{Q}}\text{Q}$ and $^{\text{R}}\text{Q}$ branches to small changes in the value assumed for the upper-state centrifugal distortion constant, D'/cm^{-1} : (b) 0, (c) 0.5×10^{-6} , (d) 1×10^{-6} ; similar effects can be achieved by subtle variations in the assumed value of A' and/or γ' .

Fig. 8 Schematic showing three possible REMPI excitation processes of SCl(X) radicals

To distinguish between schemes (a) and (b) we performed an identical rigid-rotor rotational analysis on $S^{35}Cl$ band B. For both branches ΔB appears to be *ca.* 0.033 cm^{-1} and the origin of this band is $57\,630 \pm 20\text{ cm}^{-1}$. This result puts the separation of the band origins of A and B at $590 \pm 40\text{ cm}^{-1}$. Given this separation of the two bands A and B and the previous⁸ determination of the $v = 1 - v = 0$ separation in $SCl(X)$ we strongly favour the interpretation of excitation scheme (b) over (a).

We disfavour scheme (c) because, while exciting through band A, we fail to observe any photoelectron peaks attributable to SCl on the high kinetic energy side of the already assigned $(0 \leftarrow 0 \leftarrow 0)$ peak (peak III in Fig. 4). For example, if we chose to assign the 1.263 eV peak in terms of a $(1 \leftarrow 1 \leftarrow 0)$ ionisation process then, on Franck-Condon grounds, we would expect to see a small peak to higher kinetic energies associated with a $(0 \leftarrow 1 \leftarrow 0)$ ionisation sequence. Also, if excitation scheme (c) were appropriate in this case, the observed separation of bands A and B would provide a measure of the vibrational spacing of $v' = 1 - v' = 0$ levels in the Rydberg state. Given the deduced 590 cm^{-1} separation of bands A and B, such an explanation would imply a surprisingly large disparity between the vibrational frequency of the Rydberg state and that of the ground state of the ion (685 cm^{-1}) which, given the deduced $\Delta v = 0$ propensity accompanying the ionisation process, seems unlikely.

Thus we conclude that excitation scheme (b) is most likely to be responsible for the spectra shown here. However, it should be noted that under such an excitation scheme the observation of the $^2\Pi-X\ ^2\Pi_{3/2}$ $(0-0)$ and $(0-1)$ transitions would imply that the Franck-Condon factors for $^2\Pi-X\ ^2\Pi_{3/2}$ $(1-1)$ and $(1-0)$ bands should also be reasonably favourable. The failure to observe bands assignable in these terms in our REMPI spectrum may indicate that the $^2\Pi$ ($v' = 1$) level has a significantly shorter lifetime, most probably due to predissociation.

We now return to the assignment of an adiabatic ionisation energy of SCl . Examination of the REMPI-PE spectrum recorded at $2\tilde{\nu} = 58\,359.2\text{ cm}^{-1}$ (Fig. 4) revealed an effective ionisation energy of 9.59 eV . The rotational analysis has subsequently shown that this spectrum was recorded exciting a $^Q Q$ or $^R Q$ transition with $J'' \approx 68.5$. Given the estimate of B' , a correction of 0.02 eV is needed to take account of the difference in the rotational energy between the initial state of the neutral and the final state of the cation. The uncertainty in this correction appears to be small and thus we determine a value of $9.57 \pm 0.01\text{ eV}$ for the first adiabatic ionisation energy of the SCl radical.

Having established the E_i of SCl we can use the following modified form of the Rydberg formula

$$\tilde{\nu} = E_i - \frac{R}{(n - \delta)^2} \quad (6)$$

(where R is the Rydberg constant, $109\,737\text{ cm}^{-1}$) to calculate the quantum defect, δ , associated with the newly identified $^2\Pi$ Rydberg state. Thus we obtain $(n - \delta) = 2.41$ and a value of 1.59 (assuming $n = 4$) for its quantum defect. Comparison with atomic sulfur suggests strongly that this excited state is part of the $4p$ Rydberg complex of the SCl radical. This being so, its $^2\Pi$ symmetry establishes its electronic configuration as $[^3\Sigma^-]4p\pi$.

At 9.57 eV , the E_i of SCl (in as much that it is less than that of either of the constituent atoms) is consistent with a qualitative molecular orbital picture which assigns the highest occupied molecular orbital (HOMO) in the ground-state configuration as being somewhat antibonding in character. The ground-state ion is formed by removing one electron

from this antibonding $4p$ orbital; upon ionisation we might therefore predict that the equilibrium bond length, r_e , should decrease and that the vibrational frequency, ω_e , would increase. The latter expectation is confirmed by our observation that the $v = 1 - v = 0$ level spacing in the ground-state ion is $685 \pm 30\text{ cm}^{-1}$ (*cf.* 574.6 cm^{-1} in the ground-state neutral).⁸ We have no direct measure of r_e in the ion, but our deduced rotational constant for the $^2\Pi$ Rydberg state implies that it has a bond length some 13% shorter than that of the ground-state neutral. Given that the geometries of the Rydberg state and the ground state of the SCl^+ ion are likely to be very similar, we infer that r_e does indeed contract upon ionisation.

Finally, we consider briefly what the REMPI and REMPI-PES analysis tells us about the primary photochemistry of the SCl_2 precursor molecule. Our results suggest that the near-UV photodissociation of SCl_2 , at wavelengths in the range $340\text{--}346\text{ nm}$, yields SCl radicals in the $\Omega = 3/2$ spin-orbit component of the ground state, with a markedly non-Boltzmann rotational-state population distribution encompassing a wide range of high J'' states.

The exclusive production of SCl molecules in the $\Omega = 3/2$ level is mysterious but shows remarkable parallels with previous works on SCl which have utilised the photodissociation of SCl_2 and S_2Cl_2 . Using 248 nm light and thus exciting through a different excited state of SCl_2 ,¹⁵ Tiemann *et al.*⁸ also failed to observe any transitions consistent with the existence of $SCl(X, \Omega = \frac{1}{2})$ in the photoproduct distribution.

The rotational-state distribution appears to be centred around $J'' \approx 85.5$ and is approximately Gaussian in profile. Photofragment rotational-state population distributions of this general form are not uncommon. They can arise, for example, in cases where the parent molecule (ABC) experiences a change in the interbond angle (θ) upon excitation to a state the potential-energy surface for which is repulsive along the $A-B$ coordinate. The so-called reflection principle¹⁸ has been shown to operate in such cases, yielding a rotational state population distribution in the BC products which mimics the parent ground-state bending vibrational wavefunction. Such is entirely consistent with the available data pertaining to SCl_2 . The wavelengths used in the present work fall within the second identifiable absorption band in its electronic spectrum. This broad, apparently structureless feature has been assigned¹⁵ to the $^1B_2 \leftarrow ^1A_1$ transition, associated with the orbital promotion $\{\cdots (12a_1)^1(4b_2)^1 \leftarrow \cdots (4b_2)^2\}$. The $12a_1$ orbital is strongly antibonding, so it is not unreasonable to suppose that the $^1B_2$ state is dissociative with respect to elongation of one $S-Cl$ bond. Further, preliminary calculations¹⁹ show that, in the bending coordinate, the minimum-energy configuration of the excited $^1B_2$ state occurs at $\angle ClSCl$ angles significantly greater than that of the ground state.

Conclusions

This one-colour study has revealed the formation of rotationally excited $SCl(X\ ^2\Pi)$ radicals amongst the primary products of SCl_2 photolysis at near-UV wavelengths around 343 nm . The $SCl(X)$ radicals are detected by MPI spectroscopy, resonance enhanced by an excited state at the two-photon energy. This constitutes the first reported observation of any excited electronic state of the SCl radical. Analysis of the rotationally resolved REMPI spectrum shows the excited state to have $^2\Pi$ electronic symmetry, an origin term value $\nu_0 = 58\,220 \pm 20\text{ cm}^{-1}$ measured relative to the lower ($X\ ^2\Pi_{3/2}$) component of the ground state, and a bond length *ca.* 13% shorter than that of the ground-state neutral. Quantum defect

considerations suggest that this excited state derives from the electronic configuration involving a $4p\pi$ Rydberg electron built on the $^3\Sigma^-$ ground-state ion core. Parallel REMPI-PES studies yield a value of 9.57 ± 0.01 eV for the first E_i of SCl (again measured relative to the lower, $^2\Pi_{3/2}$, spin-orbit component of the ground state), and show the vibrational level separation in the ground-state ion to be 685 ± 30 cm^{-1} (some 19% higher than the corresponding energy interval in the ground-state neutral).

We anticipate that future two-laser studies which permit decoupling of the photolysis and REMPI probing steps should prove fruitful, both in extending the available spectroscopic data base pertaining to the SCl radical and as a means of studying the product energy disposal and hence the photodissociation dynamics of the SCl_2 precursor.

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