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Spectra of the vibronic transition A–X of S_2^+ in solid neon

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Abstract

On subjecting either CS_2 or sulphur vapour in flowing neon to microwave discharge and collecting the products, we formed dilute deposits of S_2^+ in solid Ne near 5 K. The photoluminescence of S_2^+ in the system $A\ ^2\Pi_u \rightarrow X\ ^2\Pi_g$ was measured in the wavelength range 450–800 nm, and isotopically enriched samples of $^{34}S_2^+$ and $^{32}S^{34}S^+$ yielded unambiguous vibrational assignments; for $^{32}S_2^+$ up to $v'' = 12$, $\tilde{\nu}_{00} = (22260.8 \pm 1.4)$, $Y''_{1,0} = (809.0 \pm 0.6)$ and $Y''_{2,0} = -(3.50 \pm 0.04)$ cm^{-1}. In these photoluminescence spectra, two distinct progressions with separation insensitive to nuclear mass are observed, involving spin–orbital substates of the electronic ground state; the value of the spin–orbital coupling parameter A''_0 is (493 ± 2) cm^{-1}. Excitation spectra in the region 330–430 nm exhibited for $^{32}S_2^+$ a progression up to $v' = 15$ with $Y'_{1,0} = (556.0 \pm 0.4)$ and $Y'_{2,0} = -(3.21 \pm 0.03)$ cm^{-1}. With improved resolution, the splitting of most lines into doublets or triplets is attributed to the effects of S_2^+ in solid neon, being trapped in sites of multiple character. We compare our results for trapped $^{32}S_2^+$ with those reported for free $^{32}S_2^+$ in the gaseous phase, and discuss the spectral consequences of the confinement of species trapped by surrounding Ne atoms.

Keywords: Matrix isolation; Photoluminescence; S_2^+; Vibronic transition

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1. Introduction

Photoelectron spectra of S_2 yielded the first experimental information about the electronic and vibrational energy states of S_2^+ [1,2]. Although the effective spectral resolution of these measurements was only moderate (≈ 50 cm^{-1}), the analysis (of these and succeeding spectra) indicated that the electronic ground state belonged to symmetry class $^2\Pi_{g,r}$, and that two other doublet states, $A\ ^2\Pi_u$ and $B\ ^2\Sigma_g^-$, existed within the range of energies corresponding to the visible and ultraviolet spectral regions. Also according to those experiments, two quartet states, $a\ ^4\Pi_u$ and $b\ ^4\Sigma_g^-$, exist within the same energy range, < 5.2 eV.

Of the few investigations of optical spectra of S_2^+ in the gaseous phase [3–6], all have relied on emission from the state $A\ ^2\Pi_{u,r}$ to the ground electronic state; the maximum range of vibrational states was $0 \leq v' \leq 10$ and $0 \leq v'' \leq 11$ [6]. Analysis of the rotational fine structure yielded rotational parameters and characterised the vibrational states within the specified range.

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Of the few reports on the electronic spectra of molecular ions dispersed in a solid substrate formed from a noble gas, none pertain to optical spectra of S_2^+ in a condensed phase. In our experiments we not only observed photoluminescence of S_2^+ radical ions trapped in solid neon by means of the electronic transition $A \rightarrow X$, but also measured excitation spectra of this diatomic species so as to extend the range of spectral characterisation in state A. Our samples included not only natural sulphur, largely ^{32}S, but also samples enriched moderately or greatly with ^{34}S, as a means to prove conclusively the identity of the carrier of our spectra and the vibrational assignments.

2. Experimental

For experiments involving ^{32}S, we used either elemental sulphur heated to 373 K or CS_2, but our only source of ^{34}S was $C^{34}S_2$ (99% isotopic purity of S, Cambridge Isotope Laboratories, USA). In each case, we subjected the flowing gaseous mixture of the sulphur precursor with neon (molar ratio Ne:S in the range 1000–2000) to electrodeless microwave discharge at 2.45 GHz from a generator (Opthos, USA). For periods of typically 1–2 h, a discharged mixture was deposited on a copper substrate maintained at about 5 K by means of a cryogenic refrigerator (RMC LTS-1C-4.5 CM). The deposit formed about 70 mm downstream from the centre of the discharge zone.

We irradiated the deposit with the output from a dye laser (Lambda Physik, LPD3002E, Germany) pumped by an excimer laser (Lambda Physik, LPX220i, Germany) operated at 10 Hz. The emission from the sample passed through a monochromator (Jobin-Yvon, HR640, France) and was detected by a photomultiplier (Hamamatsu, R955, Japan). The resulting electrical signal was amplified and averaged with a boxcar integrator (EG and G, 4402 and 4420, USA) before being transferred to a microcomputer for further processing. The sampling procedures were controlled with this microcomputer via IEEE-488 and RS232 interfaces. The signal was averaged within a gate window 0.8–3 μs after the laser pulse (of width 10 ns); 50 laser pulses were typically averaged for each data point. For photoluminescence measurements the spectral slit width of the monochromator was about 4 cm^{-1} at 14000 cm^{-1} and 7 cm^{-1} at 25000 cm^{-1}; the scan step was 0.05–0.10 nm. We calibrated the monochromator before and after each experiment by means of a Hg lamp; the reproducibility was generally better than 0.03 nm. The precision of the wavelength measurement of a sharp line (such as a zero-phonon line) was ±1 scan step. The dyes used to measure the excitation spectra, with their corresponding spectral ranges and maximum output energy per pulse, are specified as follows: LC3590, 346–377 nm, 6 mJ; LC3690, 368–402 nm, 8 mJ; LC4090, 399–415 nm, 6 mJ; LC4200, 412–443 nm, 4 mJ; LC4400, 423–462 nm, 8 mJ; LC4700, 440–484 nm, 8 mJ. To measure the excitation spectra we set the monochromator at the wavelength of the line of maximum intensity in the photoluminescence, near 545 nm depending on the isotopic variant, and laser scanned the region in which the particular dye was useful. To ensure an adequate signal-to-noise ratio, we generally set the slits of the monochromator to pass about 13 cm^{-1}, but for special purposes we decreased the spectral band pass to 4 cm^{-1}. Although the width of the emission line from the laser was about 0.2 cm^{-1}, the interval 1.2 cm^{-1} between scan steps limited the effective resolution to the latter value, despite the much greater band pass accepted by the monochromator. As the widths of narrow lines were ≈ 3 cm^{-1}, neither the width of the laser line nor the scan step adversely affected the effective resolution of the measured spectra.

3. Results

The cryodeposit prepared with sulphur (with either elemental sulphur or CS_2 as precursor) in natural isotopic abundance and neon was illuminated with light from the dye laser at 370.7 nm. The photoluminescence exhibited two progressions of sharp lines, accompanied by broader features and clusters of partially resolvable lines, in the spectrum we measured in 0.05 nm steps within the range 400–800 nm (partial spectrum shown in Fig. 1a). When CS_2 containing sulphur greatly enriched in ^{34}S was used as a precursor, the pattern of emission was similar to that in Fig. 1a, except that the lines were shifted towards greater wavenumbers. When CS_2 with sulphur in the isotopic ratio ^{32}S:^{34}S = 1:1.2 was used to prepare a solid sample, the emission spectrum (Fig. 1b) comprised not only lines observed for samples containing only ^{32}S or ^{34}S, but also a third set of lines at intermediate positions; the wavenumbers of these three sets of lines, each of two obvious progressions, are listed in Table 1. The intervals between adjacent emission lines decrease regularly with increasing vibrational quantum number; this regularity indicates not only the precision of wavenumber measurements of all isotopic variants, but also the apparent absence of heterogeneous vibrational perturbations within the range of our measurements.

We recorded excitation spectra of our samples by measuring the emission intensity near 545 nm (the line of maximum intensity in the photoluminescence spectra shown in Fig. 1) as we scanned the incident laser beam in the region 330–430 nm in 0.02 nm steps. As in the photoluminescence spectra, we observed (Fig. 2a) for a sample containing mostly ^{32}S one progression of close doublets of interval 6–9 cm^{-1}, with intermediate clusters of lines characteristic of coupling between intramolecular and lattice motions; for another sample containing mostly ^{34}S there was a separate progression of doublets of interval 3–5 cm^{-1}. For samples containing both ^{32}S and ^{34}S in comparable proportions, besides the preceding two progressions of doublets, a further progression of triplets with inner interval ≈ 4 cm^{-1} was discernible. When we discovered these triplets in the spectrum of $^{32}S^{34}S^+$, we decreased the scan step during excitation to 0.002 nm and increased the slit width of the monochromator; under these conditions, for a single experiment in which spectra of both $^{32}S_2^+$ and $^{32}S^{34}S^+$ were produced, we discovered that within at least the range of a particular dye in the laser for excitation, doublets of the spectrum of $^{32}S_2^+$ also consisted of triplets. Parts of the latter spectrum, uncorrected for the variation of output power of the laser with the dye, appear in Fig. 2a; wavenumbers of the most intense line in each multiplet are listed in Table 2. Beyond about 28 000 cm^{-1}, the increasing width of members of these progressions precluded resolution into a doublet or triplet structure.

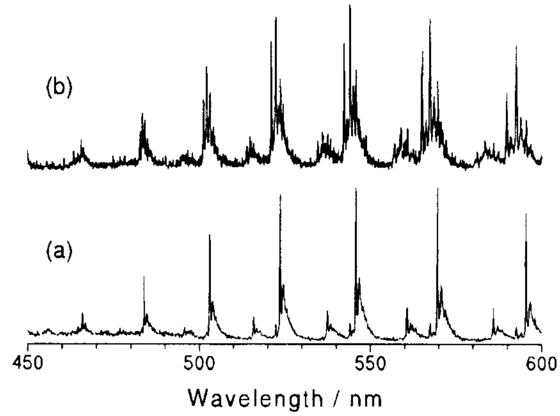

Fig. 1. Partial spectrum in the range 450–600 nm of photoluminescent emission of (a) $^{32}S_2^+$ excited at 26 976 cm^{-1} and (b) a mixture of $^{32}S_2^+$, $^{34}S_2^+$ and $^{32}S^{34}S^+$ excited at 26 915 cm^{-1}. The ordinate is emission intensity.

4. Analysis of spectra

4.1. *Identification of the carrier of the spectra*

Rotational fine structure in resolved spectra of gaseous species generally enables unambiguous identification of the carrier with the aid of information about the chemical nature of the sample. For condensed phases, the lack of such rotational structure precludes such a direct process of identification. In these circumstances we used isotopically labelled reagents to achieve the same objective.

Because in excitation spectra one distinct set of sharp lines appeared for each separate sample containing mostly ^{32}S or ^{34}S, and because only one additional set of lines appeared when we used a mixture of all three isotopic species in our sample, the carrier almost certainly contains only two S atomic centres. Because spectra associated with ^{32}S were obtained readily when we used only natural elemental sulphur as a precursor of the

Table 1
Wavenumbers (cm^{-1}) of lines in two progressions from v$' = 0$ in photoluminescence of samples of S_2^+, containing ^{32}S and ^{34}S in varying proportions, in solid Ne at 5 K

v$''$	$^{32}S_2^+$/Ne		$^{34}S_2^+$/Ne		$^{32}S^{34}S^+$/Ne	
	Line	Interval	Line	Interval	Line	Interval
First progression						
1	21 458	794	21 488	770		
2	20 664	786	20 718	767	20 688	775
3	19 878	782	19 951	758	19 913	771
4	19 096	773	19 193	752	19 142	760
5	18 323	768	18 441	745	18 382	759
6	17 555	763	17 696	741	17 623	748
7	16 792	751	16 955	733	16 875	745
8	16 041	750	16 222	726	16 130	734
9	15 291	737	15 496	720	15 396	
10	14 554	731	14 776	714		
11	13 823	720	14 062	706		
12	13 103		13 356			
Second progression						
1	20 967	793	20 998	771		
2	20 174	789	20 227	767		
3	19 385	779	19 460	759	19 422	771
4	18 606	773	18 701	749	18 651	760
5	17 833	766	17 952	746	17 891	756
6	17 067	759	17 206	739	17 135	743
7	16 308	750	16 467	730	16 392	748
8	15 558	750	15 737	726	15 644	
9	14 808	737	15 011	718		
10	14 071	730	14 293	713		
11	13 341		13 580			

dilute component in mixtures with neon, atoms of no other element than sulphur are likely to be present in the carrier: stable compounds of neon have almost no precedent. Therefore, the carrier of the spectrum appears to consist of only two atomic centres, both S. The spectrum could not belong to neutral S_2 [7–9] because we detected characteristic spectral features of the latter species in the visible and ultraviolet regions of the same experiments, or in experiments without electric discharge of the flowing gaseous mixture deposited at 5 K. The vibrational spectral patterns that we measured for microwave-discharged samples containing only ^{32}S show, however, a great resemblance to those of S_2^+ with respect to emission in the gaseous phase [6]. For all these reasons, plus the consistency of our values of $Y_{1,0}$ and $Y_{2,0}$ with those derived for $^{32}S_2^+$ in the gaseous phase (see the vibrational analysis in Section 4.2), we assign the sharp lines reported in Tables 1 and 2 to the diatomic sulphur radical ion S_2^+ in its three isotopic variants. We assigned the many other broader lines or clusters of lines within the same spectral region, accompanying but less intense than the adjacent sharp and more isolated lines, to transitions involving coupling of the vibrational motion of various S_2^+ species with vibrations (phonons) of the neon lattice. The latter spectral features are of no interest in the present context.

Excitation and photoluminescence spectra were most intense from the region of the deposited sample in which the light from the gaseous discharge in the flowing mixture of Ne and precursor

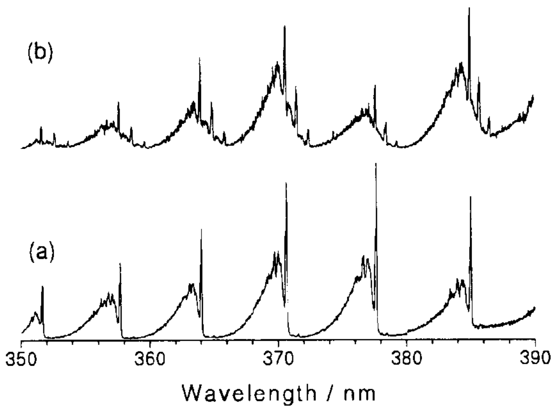

Fig. 2. Partial excitation spectra of (a) $^{32}S_2^+$ detected at 18 323 cm^{-1} and (b) a mixture of $^{32}S_2^+$, $^{34}S_2^+$ and $^{32}S^{34}S^+$ detected at 18 382 cm^{-1}; the dye laser was scanned over the range 350–390 nm. The dye was changed near 380 nm and the spectra were not normalised to the output profile of the dye laser. The ordinate is emission intensity.

reached the frozen deposit. It is therefore likely that S_2^+ ions were produced not only in the gaseous phase, but also by means of photoionisation of neutral S_2 molecules, known to be present within the solid deposit according to their spectra.

4.2. Vibrational analysis

According to the assumption that the carrier of the spectral lines is S_2^+ in the isotopic variant specified in Tables 1 and 2, we simultaneously fitted the wavenumbers of the most intense lines of each multiplet in the photoexcitation spectra and the first progression of the photoluminescence spectra, in the upper part of Table 1, of each variant to a function of the form

$$\tilde{\nu} = T_e + Y'_{1,0}(v' + 1/2) + Y'_{2,0}(v' + 1/2)^2 - Y''_{1,0}(v'' + 1/2) - Y''_{2,0}(v'' + 1/2)^2 \qquad (1)$$

with $v'' = 0$ and $v' \geq 1$ for excitation spectra or $v' = 0$ and $v'' \geq 2$ for photoluminescence spectra. The values of the resulting parameters T_e, $Y'_{1,0}$, $Y'_{2,0}$, $Y''_{1,0}$ and $Y'_{2,0}$ appear in Table 3; each associated uncertainty denotes a single estimated standard error. To evaluate $\tilde{\nu}_{00}$ instead of T_e we refitted the same data to an equation of the form of Eq. (1) that lacked the addend of 1/2 to both v′ and v″ in all instances. For the second progression of photoluminescence, we fitted only the data in the lower section of Table 1 to a relation like Eq. (1), but lacking terms in $Y'_{k,0}$, $k = 1$ or 2; the addend of 1/2 was included in the evaluation of $Y''_{1,0}$ and $Y''_{2,0}$, but not in the calculation of $\tilde{\nu}_{00}$.

Table 2
Wavenumbers (cm^{-1}) of lines measured in excitation spectra from $v'' = 0$ of samples of S_2^+, containing ^{32}S and ^{34}S in varying proportions, in solid Ne at 5 K

v″	$^{32}S_2^+$/Ne		$^{34}S_2^+$/Ne		$^{32}S^{34}S^+$/Ne	
	Line	Interval	Line	Interval	Line	Interval
2	23 353	537	23 324	521	23 340	527
3	23 890	529	23 845	515	23 867	
4	24 419	524	24 360	509		
5	24 943	519	24 869	504	(24 907)	511
6	25 462	510	25 373	497	25 418	508
7	25 972	506	25 870	491	25 926	495
8	26 478	498	26 361	485	26 421	494
9	26 976	492	26 846	479	26 915	487
10	27 468	485	27 325	473	27 402	475
11	27 953	480	27 798	466	27 877	475
12	28 433	471	28 264		28 352	
13	28 904	465				
14	29 369	459				
15	29 828					

Table 3
Spectral parameters (cm^{-1}) derived from analysis of photoluminescence and excitation spectra of $^{32}S_2^+$, $^{34}S_2^+$ and $^{32}S^{34}S^+$ in solid neon, with data of $^{32}S_2^+$ in the gaseous phase for comparison

Species	$^{32}S_2^+$(solid Ne)	$^{32}S_2^+$(gas)[a]	$^{34}S_2^+$(solid Ne)	$^{32}S^{34}S^+$(solid Ne)
Excitation [b]				
T_e	22 387.3 ± 1.8	22 345.45 ± 0.03	22 388.1 ± 0.9	22 383.9 ± 2.7
$\tilde{\nu}_{00}$	22 260.8 ± 1.4	22 218.80 ± 0.02	22 265.4 ± 0.7	22 260.3 ± 2.0
$Y'_{1,0}$	556.0 ± 0.4	552.635 ± 0.011	538.7 ± 0.3	548.6 ± 0.7
$Y'_{2,0}$	−3.21 ± 0.03	−3.1365 ± 0.0024	−2.98 ± 0.02	−3.15 ± 0.05
Photoluminescence				
First progression [b]				
$Y''_{1,0}$	809.0 ± 0.6	806.10 ± 0.01	784.1 ± 0.3	795.9 ± 0.9
$Y''_{2,0}$	−3.50 ± 0.04	−3.3971 ± 0.0018	−3.20 ± 0.02	−3.31 ± 0.08
Second progression [c]				
$\tilde{\nu}_{00}$	21 767.8 ± 1.5	21 746.70 ± 0.027	21 776.1 ± 1.1	21 764.0 ± 14.1
A''_0	493.1 ± 2.0	472.100 ± 0.034	489.4 ± 1.3	496.3 ± 14.2
$Y''_{1,0}$	807.7 ± 0.6	806.10 ± 0.01	785.0 ± 0.5	794.2 ± 6.0
$Y''_{2,0}$	−3.47 ± 0.05	−3.3971 ± 0.0018	−3.33 ± 0.04	−3.27 ± 0.49

[a] Data from [4].

[b] Parameters were derived by a simultaneous fit of data in the upper section of Table 1 and excitation spectral lines in Table 2; see text.

[c] Parameters were derived by fitting data in the lower section of Table 1; see text.

The range of standard deviations of fits was 0.7–3.0 cm^{-1}, reflecting both the number and precision of data, and consistent with the effective spectral resolution of our measurements; standard deviations are larger for $^{32}S^{34}S^+$ than for either $^{32}S_2^+$ or $^{34}S_2^+$ for two reasons: because the data are sparser, and because the spectra contained many sharp lines and phonon wings of the latter two species in addition to the expected spectral features of $^{32}S^{34}S^+$.

5. Discussion

The electronic transition of S_2^+ in the spectral region investigated by us is well characterised as $A\ ^2\Pi_{u,r}$–$X\ ^2\Pi_{g,r}$ according to analyses of spectra of gaseous samples, for which effects associated with rotational fine structure enable definitive specification of symmetry classes of combining states [3,4]. Although the $a\ ^4\Pi_u$ state, of intermediate energy to the A and X states, was deduced from photoelectron spectra [1], we found no evidence of it in our optical spectra. In both the ground state $X\ ^2\Pi_{g,r}$ and excited state $A\ ^2\Pi_{u,r}$, S_2^+ dissociates into an atom S ^3P and an ion S^+ ^4S. Thus, the molecular electronic transition is weakly allowed according to the electric dipole type; such transitions have typical oscillator strengths of $\approx 10^{-3}$, with which our measured radiative lifetime 1.0 ± 0.2 μs of S_2^+ in solid neon is fully consistent.

The reduced molecular mass of a molecular ion is given by $\mu_r = M_aM_b/(M_a + M_b - m_e)$, where M_a and M_b are the atomic masses of neutral atoms, and m_e is the electronic mass. Application of appropriate ratios of the reduced molecular masses to values of $Y_{1,0}$ and $Y_{2,0}$ of both electronic states of $^{32}S_2^+$, $^{34}S_2^+$ and $^{32}S^{34}S^+$ in Table 3 indicates satisfactory consistency between the independently fitted values. Despite the dissimilar models in fits of the first and second progressions, the agreement between $Y''_{1,0}$ and $Y''_{2,0}$ for corresponding parameters of a particular isotopic variant is comparable with the combined standard errors of all three isotopic variants.

Because both the X and A states of S_2^+ consist of substates $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ separated according to the extent of spin–orbital interaction, optical transitions between substates with $\Omega = 1/2$ and $\Omega = 3/2$ might allow their detection in our spectra.

We measured two progressions separated by 493 ± 2 cm^{-1} for $^{32}S_2^+$, 489 ± 1 cm^{-1} for $^{34}S_2^+$ and 496 ± 14 cm^{-1} for $^{32}S^{34}S^+$; these values are the differences between two values of $\tilde{\nu}_{00}$ in photoluminescence spectra of each isotopic species in Table 3. The intensity of the lines in the second progression was about a quarter of that of the corresponding lines in the progression at greater wavenumber. These differences in wavenumber between the apparent origins of the two progressions appear essentially constant within experimental uncertainty. Thus, they are independent of molecular mass, and can be related to the spin–orbital interaction, not a vibrational effect that is expected to exhibit significant variation with reduced mass similar to that of any parameter $Y_{k,0}$ in Table 3. The magnitudes of these three values are significantly larger than the known value of A_0'' of the X state in the gaseous phase, ≈ 472.1 cm^{-1}, and much larger than $A_0' \approx 12.3$ cm^{-1} for the A state of $^{32}S_2^+$ [6]. Confinement of S_2^+ by surrounding neon in our solid samples evidently increased the effective splitting of substates of the electronic ground state by ≈ 20 cm^{-1}. Thus, wavenumbers in the upper part of Table 1 and data for the first progression in Table 3 pertain to the transition $A\ ^2\Pi_{u,1/2}$ $(v' = 0) \rightarrow X\ ^2\Pi_{g,1/2}$ $(v'' \geq 1)$, whereas wavenumbers in the lower part of Table 1 and data for the second progression in Table 3 pertain to the transition $A\ ^2\Pi_{u,1/2}$ $(v' = 0) \rightarrow X\ ^2\Pi_{g,3/2}$ $(v'' \geq 1)$. Insignificant variation of the intensity distribution in the measured photoluminescence with the wavenumber of excitation (or of absorption by S_2^+) above 23 256 cm^{-1} leads to the following deduction: a rapid intramolecular radiationless relaxation within both manifolds of the electronic substates $A\ ^2\Pi_{u,1/2}$ and $A\ ^2\Pi_{u,3/2}$ to the vibrational state $v' = 0$ of substate $A\ ^2\Pi_{u,1/2}$, from which radiative relaxation occurred with a lifetime of 1.0 ± 0.2 μs to various vibrational states of both substates $X\ ^2\Pi_{g,1/2}$ and $X\ ^2\Pi_{g,3/2}$, $\Delta\Omega = 0$ and $+1$, according to regular distributions depicted in Fig. 1.

The small splitting of some lines in the excitation spectrum might correspondingly indicate the presence of two substates in the excited state $A\ ^2\Pi_{u,r}$. However, this splitting of $\approx 8 \pm 1$ cm^{-1} is significantly smaller than the value $A_0' \approx 12.3$ cm^{-1} in the gaseous phase [4] and, in addition, under conditions of enhanced resolution we observed not merely doublets but triplets. These triplets were evident in our spectra of $^{32}S^{34}S^+$ throughout the measured excitation spectrum from $v' = 2$ to $v' = 12$, except at 24 000–25 000 cm^{-1}. Within the latter range, the small radiant power with the available laser dye precluded measurements at sufficient resolution to observe such a triplet near 24 907 cm^{-1} or indeed any signal near 24 400 cm^{-1}. The origin of these triplets became clear when we set the laser to excite in turn each member of the triplet of $^{32}S_2^+$ near 27 470 cm^{-1} and scanned the monochromator to record photoluminescence; the resulting spectra are given in Fig. 3a–c, in which, despite the moderate signal-to-noise ratio, it can be discerned that excitation at one wavenumber of a member of each triplet in the excitation spectrum produces only one distinct line in the photoluminescence. The corresponding phenomenon was observed in the excitation spectrum when we both decreased the scan step of excitation from 0.02 to 0.002 nm,

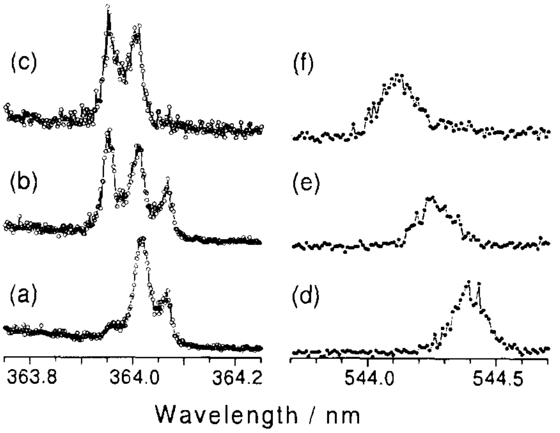

Fig. 3. Excitation and photoluminescence spectra of $^{32}S_2^+$; (a)–(c) excitation spectra recorded when the dye laser was scanned over the indicated range, while the monochromator through which the emission was measured was set at (a) 18 325.1 cm^{-1} with spectral slit width 4.3 cm^{-1}, (b) 18 328.4 cm^{-1} with spectral slit width 13 cm^{-1}, and (c) 18 330.8 cm^{-1} with spectral slit width 4 cm^{-1}; (d)–(f) photoluminescence when the monochromator (with spectral slit width 4.2 cm^{-1}) was scanned through the indicated range, while the sample was irradiated at (d) 27 466.7, (e) 27 470.1 and (f) 27 474.5 cm^{-1}.

and decreased the spectral slit width of the monochromator passing the photoluminescent signal from 13 to 4.3 cm^{-1}, shown in Fig. 3d–f; at the former slit width all three members of the triplet appear, whereas with the narrow slit only two lines have significant intensity, either outer member with the centre member of the triplet. This evidence is consistent with the molecular ions S_2^+ becoming trapped in sites of three distinct kinds within solid neon deposited at 5 K. The wavenumbers presented in Tables 1 and 2 are those of the most intense member of each multiplet corresponding to S_2^+ molecules being trapped in the most stable site. For this reason, the spectral parameters in Table 3 were calculated on the basis of the most intense lines within each doublet or triplet.

Although the nature of these three sites for trapped S_2^+ is unknown, the effective size of the S_2^+ molecular ion (assumed to be about $2R_e$ or 3.6×10^{-10} and 4.0×10^{-10} m for the X and A states respectively) is comparable with the diameter [10] (3.16×10^{-10} m) of a substitutional site in a neon lattice, or equivalent to the effective diameter of a Ne atom. Hence, S_2^+ probably occupies a substitional site within the lattice in the most stable state. Additional repulsion between the expanded molecule in the excited electronic state and the surrounding lattice is consistent with increased values of both $Y'_{1,0}$ and the origin (T_e or $\tilde{\nu}_{00}$ in Table 3); any stabilisation by the surrounding neon atoms is more than offset by this repulsion. Whether the other less stable sites reflect a different orientation of S_2^+, the presence of lattice defects near the guest ion, or a crystal structure of neon other than face-centred cubic remains an open question. The slightly increased value of the origin of the electronic transition of S_2^+ in solid neon, relative to that of free molecules (Table 3), is contrary to the trend of generally decreased transition wavenumbers at the electronic origin of trapped neutral diatomic molecules [11], but is consistent with such a site of greater repulsion in the excited state. For this trend to also apply to S_2^+ would imply errors of vibrational assignments in the spectra of gaseous samples. However, the similarity between the corresponding assignments for solid and gaseous samples makes such errors unlikely. Because our samples were highly dilute (molar fraction of guest species $\approx 10^{-3}$) and because S_2^+ ions are expected to be reactive towards, or to interact strongly with, almost any chemical species other than neon, it appears unlikely that the S_2^+ ions we detected by means of their narrow spectral lines occupy a site in the lattice adjacent to atomes other than neon.

The constancy of T_e, within experimental error, of three isotopic variants of S_2^+ in solid neon provides proof of correct vibrational assignments, even though lines of the transition $v' = 0 – v'' = 0$ were too weak to be detected in either photoluminescence or excitation spectra, and likewise $v' = 1 \leftarrow v'' = 0$ in excitation spectra. For the corresponding vibrational transitions, shifts between band centres for $^{32}S_2^+$ in the gaseous phase and measured lines of samples of $^{32}S_2^+$ in solid neon are small relative to the spacing within a vibrational progression. Thus, our spectra of isotopic variants not only define the carrier of the spectra but also positively establish the vibrational assignments.

Comparison of the $Y''_{1,0}$ values of $^{32}S_2^+$ in solid neon and as free molecules (Table 3) indicates only marginal variations, not much larger than the standard errors of these parameters. The values of $Y''_{2,0}$ and $Y'_{2,0}$ for our solid samples differ, outside the precision of the measurements, from the values for free molecules, not least because analysis of the data of free molecular ions involved a further term containing $Y_{3,0}$ in both states; for this reason, the fitted values are not comparable. In contrast with the behaviour for $Y''_{1,0}$, for trapped $^{32}S_2^+$, $Y'_{1,0} \approx 556.0$ cm^{-1} is increased relative to the value (552.6 cm^{-1}) of the free molecular ion; the significance of this increase is confirmed by the agreement of directly calculated $Y'_{1,0}$ values of $^{34}S_2^+$ and $^{32}S^{34}S^+$ with values predicted from $Y'_{1,0}$ of $^{32}S_2^+$ by means of ratios of appropriate reduced masses. Such an increase in $Y'_{1,0}$ for the trapped ion is plausible, because in the excited state both the bond length at equilibrium (R_e) and classical amplitudes of vibration are increased relative to the electronic ground state; the repulsive interaction between guest molecular ions and surrounding neon atoms is then expected to be larger in the latter state.

Although our intramolecular vibrational parameters provide no direct measurement of this interaction, the proximity of neon is envisaged to decrease the intramolecular potential-energy function, and hence to increase $Y'_{1,0}$. The narrowness of the measured lines attests to the reproducibility of the molecular environments. The effects of the confined environment on the spectral parameters, namely to increase T_e or $\tilde{\nu}_{00}$ by about 42 cm^{-1} and $Y'_{1,0}$ by about 3.4 cm^{-1}, are minor and comparable with corresponding effects discernible for neutral S_2 [5]. This is despite the fact that one might expect a larger electrostatic or multipolar interaction between a molecular ion S_2^+ and its confining atoms of neon than between the neutral nonpolar molecule S_2 and a similar environment. Estimates of the dissociation energy according to the approximate relation $|Y_{1,0}^2/(4Y_{2,0})|$ indicate no significant variation of this property of the A state between the free molecular ion and the ion trapped in solid neon. Although we extended measurements of the vibrational states of $^{32}S_2^+$ in solid neon beyond those reported for the free molecule [6], we were unable to approach closely the dissociation limit of the state $A\ ^2\Pi_{u,r}$, expected at about 43 300 cm^{-1}. This was partly because neutral S_2 (and perhaps also other sulphur species), inevitably present in our samples in solid neon [7–9] according to the method of preparation, interfered with spectral observations above 31 000 cm^{-1}. Comparison of the intervals between adjacent vibrational states of $^{32}S_2^+$ as a free molecule [4] and of $^{32}S_2^+$ trapped in solid neon (Tables 1 and 2) indicates only a slightly distorted intramolecular potential energy for electronic states X and A within the range of our measurements. As our data pertain only to vibrational states of less than half the dissociation limits of the free species, we gained no information about the prospective existence of a large barrier in the asymptotic limit of the intramolecular potential energy in each electronic state of the guest species S_2^+ caused by neon atoms present as solid host.

6. Conclusion

Relatively few spectral data exist on the electronic and vibrational properties of molecular ions dispersed in samples of solid noble gases. In the course of the present work we extended the range of known vibrational data of $^{32}S_2^+$ from the gaseous phase and complemented them with corresponding measurements on $^{34}S_2^+$ and $^{32}S^{34}S^+$, also trapped in solid neon. The data of these isotopic variants not only enable a definitive assignment of many sharp spectral features in photoluminescence and excitation spectra to S_2^+, but also provide confirmation of the subtle effects of the environment of solid neon on the essentially intramolecular properties of trapped molecular ions. A notable result is that, relative to properties of the free molecular ions in the gaseous phase, the spin–orbital interaction of S_2^+ in solid neon increased slightly for the electronic ground state; the energy difference T_e between the two states also increased. It is clearly demonstrated that the S_2^+ in solid neon was trapped in different types of sites.

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