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Experimental and theoretical study of the double ionization of the sulphur hexafluoride molecule to singlet and triplet electronic states of its dication

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Abstract

The results of a combined experimental and theoretical study of the double ionization of sulphur hexafluoride are reported. Double-charge-transfer (DCT) spectroscopy was used in the experimental investigation. Double-electron-capture (DEC) reactions, on which DCT spectroscopy is based, are known to be subject to spin conservation. Consequently, double-ionization energies to singlet and triplet electronic states of SF_6^{2+} were measured by using H^+ and F^+ projectile ions, respectively. In the theoretical investigation, ADC(2) Green's function calculations indicated a high density of singlet and triplet electronic states for SF_6^{2+}. It was found, however, that groups of states could be identified that were well separated from adjacent groups. The average double-ionization energies (DIEs) for these groups are in good agreement with those measured. The combined experimental and theoretical approach has thus provided a considerably improved understanding of the double ionization of the SF_6 molecule. (Int J Mass Spectrom 185/186/187 (1999) 651–662) © 1999 Elsevier Science B.V.

Keywords: Measured; Calculated; Double-ionization energies; SF_6

1. Introduction

Sulphur hexafluoride is a highly efficient insulator of high-voltage equipment, and is widely used in the electrical transmission industry. It has a high single-ionization energy [1,2], but its ability to inhibit electrical discharges is mainly dependent on its large cross section for electron capture. Ionization of SF_6 does not lead to the formation of stable SF_6^+ ions [3]. The single-ionization energies to the ground and electronically excited states of SF_6^+ have, however, been measured by photoelectron spectroscopy [1,2]. An experimental study of the double ionization of SF_6 was carried out by Griffiths and Harris in 1988 [4] using double-charge-transfer (DCT) spectroscopy. The lowest double-ionization energy measured was 38.9 ± 0.5 eV with some evidence being obtained of one, or possibly two, electronically excited states of SF_6^{2+} between 38.9 and 44 eV. The signals obtained were very low, however, and signal averaging over a period of 4 h was required to obtain satisfactory spectra. The reason for the low signals became apparent as a result of subsequent studies. DCT spectroscopy is based on a double-electron-capture (DEC)

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Dedicated to Professor Michael Bowers on the occasion of his 60th birthday.

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reaction in which a fast-moving singly charged positive ion acquires two electrons in a collision with the molecule under investigation. The reaction can be represented by

$$A^+ + M \rightarrow A^- + M^{2+} \tag{1}$$

in which A^+ is a general representation of the positive ion and M that of the molecule. The endoergicity, ΔE, of the reaction is given by

$$\Delta E = \mathrm{IE}_2(M) - E(A^+ \rightarrow A^-) \tag{2}$$

where $\mathrm{IE}_2(M)$ is the double-ionization energy of M, and $E(A^+ \rightarrow A^-)$ is the energy released when A^+ converts to A^-. Two theoretical studies [5,6] suggested that a “reaction window” of endoergicities exists outside of which the probability of DEC reactions taking place is very small. Neither study predicted the width of the window or its upper and lower limits. These were investigated in a DCT spectroscopy study of CH_3Br [7]. Different projectile ions were used, thus changing the quantity $E(A^+ \rightarrow A^-)$ in Eq. (2). From the results of that study, it was concluded that for CH_3Br a reaction window exists between endoergicities of approximately 8 and 22 eV. Whereas this particular window is probably unique to CH_3Br, it has been found in numerous studies of organic molecules that 8 and 22 eV are probably quite close to the lower and upper limits, respectively, of their windows [8]. If those limits apply to SF_6, it can be seen why the negative-ion signals in the DCT spectroscopy study were so weak. OH^+ was the projectile ion used; for it, the quantity $E(OH^+ \rightarrow OH^-)$ is approximately 14.8 eV so $\Delta E \cong 38.9–14.8 = 24.1$ eV, i.e. just outside the upper limit of 22 eV, implying that the probability of the DEC reaction would be low. With the knowledge that now exists about the reaction window, one can speculate that for the study of the double ionization of SF_6, it would have been better to have used a projectile ion such as F^+ for which $E(F^+ \rightarrow F^-)$ is about 20.8 eV. Thus, for a DEC reaction of F^+ with SF_6 the ΔE would be 18.1 eV, i.e. well within the window.

In this article, the results of a considerably more detailed study of the double ionization of SF_6 are reported. For the DCT spectroscopy studies, a spectrometer [9] was used which has a translational-energy resolving power much higher than that used in the previous study [4]. The F^+ projectile ion was used in an attempt to obtain significant negative-ion signals and to probe double-ionization energies to higher-lying states. There is ample evidence [8] that spin is conserved in DEC reactions. For a molecule such as SF_6, which has a singlet ground state, DEC reactions with F^+ will populate triplet states of SF_6^{2+}. On the other hand, the use of H^+ will populate singlet states of the dication. In the present study, therefore, F^+ and H^+ were used as projectile ions in order to obtain as much information as possible about the electronic structure of SF_6^{2+}. To complement the experimental work, a theoretical study has been undertaken in which double-ionization energies to singlet and triplet states of SF_6^{2+} have been calculated. Comparison of experimental and computed data should give a deeper insight into the electronic transitions that give rise to the spectral peaks.

2. Experimental

A Finnigan 8230 mass spectrometer [10] which has been modified [9] for DCT spectroscopy was used in the experimental studies. It has reversed geometry, i.e. the magnet is situated between the source and the electric sector. The SF_6 molecules were introduced into a collision-gas cell located close to the focal plane between the magnet and electric sector. The projectile ions were generated in the source, F^+ by electron ionization of CF_4, and H^+ by electron ionization of H_2O. After acceleration to 3 keV translational energy, the ions were mass selected by the magnet, and passed through the collision-gas cell where a fraction of them underwent DEC reactions to generate F^- and H^- ions. The voltages applied to the electric sector’s plates were scanned over a preset range and the negative-ion currents recorded at the detector. Repeated scans over the same range were acquired using a Keithley data-acquisition system; this improved the signal-to-noise ratios of the currents recorded.

To determine $IE_2(SF_6)$ values from the peak positions in the spectra, it is necessary to obtain a peak position that corresponds to a known DEC reaction, i.e. for which the double-ionization energy is known. This is done by obtaining a DCT spectrum with xenon in the collision-gas cell. If the translational energy of the projectile ion is denoted by E_p, and the translational energy of the negative ion generated in the DEC reaction by $E_n(\mathrm{Xe})$, then

$$E_p - E_n(\mathrm{Xe}) = \mathrm{IE}_2(\mathrm{Xe}) - E(A^+ \rightarrow A^-) \tag{3}$$

where A^+ now represents either F^+ or H^+. For a peak in the negative-ion spectra obtained with SF_6 in the cell, the relevant equation is

$$E_p - E_n(\mathrm{SF_6}) = \mathrm{IE}_2(\mathrm{SF_6}) - E(A^+ \rightarrow A^+) \tag{4}$$

If E_p is kept constant, subtracting Eq. (4) from Eq. (3) gives

$$E_n(\mathrm{SF_6}) - E_n(\mathrm{Xe}) = \mathrm{IE}_2(\mathrm{Xe}) - \mathrm{IE}_2(\mathrm{SF_6}) \tag{5}$$

from which $IE_2(SF_6)$ can be determined since $IE_2(Xe)$ is known [11] and $E_n(\mathrm{SF_6}) - E_n(\mathrm{Xe})$ can be measured from the spectra. This calibration procedure using xenon gas was carried out before and after each DCT spectrum recorded for SF_6.

3. Theoretical

A theoretical interpretation of the observed double-ionization energies requires predictions to be made of the vertical energy differences between the initial neutral molecule ground state and the final dication states that are the stationary states of the doubly charged ion with the initial geometric structure. A straightforward approach would be to perform separate calculations of the energies of the initial state and of each final state of interest, but an alternative, much less computationally demanding procedure is to calculate the energy differences directly using a propagator method. Information required for the description of the double-ionization process is contained in the *pp* propagator, the equal-time two-particle Green's function for the N electron neutral molecule with both particles (electrons) created simultaneously at time t', and destroyed simultaneously at time t''. Matrix elements of the Fourier transform of the *pp* propagator for $t'' < t'$ take the form

$$\Pi^{(-)}_{rs,tu}(\omega) = \sum_{m \in (N-2)} \frac{X^{(m)}_{rs} X^{(m)*}_{tu}}{E^{N-2}_m - E^N_0 - \omega - i\varepsilon} \tag{6}$$

with $\varepsilon = 0^+$; this exhibits a pole wherever ω coincides with a double-ionization energy. Here, r, s, t, u can be self-consistent field (SCF) molecular orbitals and m runs over all the stationary states of the $(N - 2)$ electron dication. The algebraic diagrammatic construction (ADC) method [12] is based on the observation that a unitary transformation converts the closure sums over the dication eigenstates m into sums over the "main" two-hole ($2h$) configurations and "satellite" configurations [$3h1p$, $4h2p$, etc. which are $2h$ configurations with various degrees of particle–hole shake up (ph)] that may be constructed from the SCF molecular orbitals. The diagonal matrix with energy-difference elements $E^{N-2}_m - E^N_0$ is then transformed into a matrix $\mathbf{K} + \mathbf{C}$ in the configuration basis. $\mathbf{K} + \mathbf{C}$ may be constructed explicity in terms of the energies of, and two-electron integrals over, the SCF molecular orbitals, using a Feynman diagrammatic expansion of $\Pi_{rs,tu}$ as reference so that all contributions up to a desired order in perturbation theory (**K** is the diagonal zeroth-order matrix, **C** arises from higher order terms) are included [12]. The attractive feature of the ADC method is that the choice of the SCF configuration basis is optimally compact, in the sense that to second or third order in perturbation theory the only nonzero off-diagonal matrix elements of $\mathbf{K} + \mathbf{C}$ are between $2h$ and $3h1p$ configurations, so that the desired energy differences are eigenvalues of a $\mathbf{K} + \mathbf{C}$ matrix of dimension equal to the number of those configurations [12]. Strictly in the ADC(2) approximation, terms of up to second order in two-electron interaction integrals are included in the $2h$–$2h$ matrix elements, and up to first order in the $2h$–$3h1p$ matrix elements, whereas the $3h1p$–$3h1p$ matrix elements are of order zero, taking the form

$$K_{ijkp,ijkp} = \varepsilon_p - \varepsilon_i - \varepsilon_j - \varepsilon_k \tag{7}$$

where i,j,k denote SCF molecular spin orbitals occupied in the neutral molecule, p denotes an initially unoccupied one, and ε_i denotes the SCF energy of i. However, an acceptable quantitative description of the double ionizations requires that account be taken of the ADC(3) first-order contributions to the $3h1p$–$3h1p$ satellite matrix elements [12,13]. The diagonal first-order satellite matrix elements of **C** are of significant magnitude, typically a few eV, and reflect the pairwise interactions associated with excitation of a satellite configuration;

$$\mathbf{C}_{ijkp,ijkp} = (ij\|ij) + (jk\|jk) + (ki\|ki) - (ip\|ip) - (jp\|jp) - (kp\|kp) \tag{8}$$

with $(rs\|tu) = (rt|su) - (ru|st)$, and $(rs|tu) = \int \varphi_r(1)\varphi_s(1)|\mathbf{r}_1 - \mathbf{r}_2|^{-1}\ \varphi_t(2)\ \varphi_u(2)\ d\Omega_1\ d\Omega_2$ the coulomb integral over the space and spin coordinates of electrons 1 and 2 in the wave functions of the molecular spin orbitals. The expressions for the off-diagonal first-order satellite matrix elements of **C** are analogous [12] but tend to have much smaller magnitude. Previous applications of the ADC(2) method to double ionization have employed these matrix elements in the subspace of satellite configurations. The dimensions of the **K** + **C** matrices, up to a few thousand for the relatively small molecules studied, allowed the straightforward determination in each case of the lowest few score eigenvalues by established diagonalization procedures, the extra labour of setting up the matrix elements of **C** in the satellite configuration subspace not being excessive.

However, such an ADC(2) calculation of the double ionizations of the SF_6 molecule, which has 48 valence electrons, is much less feasible even with one of the modest split-valence bases that have proved acceptable in ADC(2) calculations for smaller molecules. SF_6 exhibits a high degree of spatial symmetry and it is straightforward computationally to employ the largest Abelian subgroup D_{2h} of its octahedral symmetry group O_h to block diagonalize **K** + **C** into eight parts. Also, spin symmetry enables further block diagonalization into singlet and triplet matrices, so that **K** + **C** may be blocked into 16 separate matrices. Nevertheless, each of these, for SF_6 in the basis used here, has dimensions of at least 5×10^4, which would require the computation of a very large number of matrix elements, and result in a corresponding difficulty in calculating the required eigenvalues and their eigenvectors.

Table 1
Energies of the occupied valence and lowest unoccupied SCF/6-311G* molecular orbitals (MO) of SF_6, calculated as described in the text

MO	ε/eV
$4a_{1g}$	−50.55
$3t_{1u}$	−46.89
$2e_g$	−45.43
$5a_{1g}$	−30.38
$4t_{1u}$	−25.45
$1t_{2g}$	−22.87
$3e_g$	−20.18
$1t_{2u}$	−20.09
$5t_{1u}$	−19.64
$1t_{1g}$	−18.85
$6a_{1g}$	3.36
$6t_{1u}$	7.23
$7t_{1u}$	9.49
$7a_{1g}$	13.52

In a recent implementation of the ADC(2) *ph*-propagator method for calculation of the electronic excitation energies of the CO molecule, Trofimov and Schirmer [14] encountered analogous **K** + **C** matrices of dimension greater than 10^4 and therefore investigated a “diagonal” approximation in which the many small off-diagonal satellite **C** matrix elements are set to zero. The ADC(2) matrices then exhibit the sparse structure characteristic of the strict ADC(2) approximation (in which only the diagonal satellite matrix elements of **K** are nonzero) but also retain the significant first-order diagonal satellite matrix elements of **C** which improve the agreement with experiment substantially. It was found [14] that the introduction of the diagonal approximation resulted in acceptable increases, no more than 0.2 eV, in the predicted excitation energies. The benefits of the diagonal approximation are both a large reduction in the number of matrix elements to be calculated, together with a consequent reduction in the computational

Table 2
Double-ionization energies (DIE) to singlet states of SF_6^{2+}, calculated with the ADC(2) propagator method using the “diagonal” approximation described in the text

Term	DIE/eV	ΔE/meV	Main/%	Leading configuration weights
$^1T_{2g}$	36.59	33	83	70% $1t_{1g}^{-2}$
^1E_g	36.91	6	83	61% $1t_{1g}^{-2}$
$^1A_{1g}$	36.93	–	84	60% $1t_{1g}^{-2}$
$^1A_{1u}$, ^1E_u	37.19	27	83	42% $1t_{1g}^{-1}\ 5t_{1u}^{-1}$, 38% $1t_{1g}^{-1}\ 1t_{2u}^{-1}$
$^1T_{1u}$, $^1T_{2u}$	37.76	32	82	43% $1t_{1g}^{-1}\ 5t_{1u}^{-1}$, 37% $1t_{1g}^{-1}\ 1t_{2u}^{-1}$
$^1T_{2g}$	38.60	29	83	42% $5t_{1u}^{-2}$, 28% $5t_{1u}^{-1}\ 3e_g^{-1}$, 12% $5t_{1u}^{-1}\ 1t_{2u}^{-1}$
$^1A_{2g}$	38.79	–	84	52% $5t_{1u}^{-1}\ 1t_{2u}^{-1}$, 32% $1t_{1g}^{-1}\ 1t_{2g}^{-1}$
$^1T_{1g}$	38.80	6	83	55% $5t_{1u}^{-1}\ 1t_{2u}^{-1}$, 26% $1t_{1g}^{-1}\ 3e_g^{-1}$
^1E_g	38.84	6	84	32% $1t_{1g}^{-1}\ 1t_{2g}^{-1}$, 20% $1t_{2u}^{-2}$, 17% $5t_{1u}^{-2}$, 12% $5t_{1u}^{-1}\ 1t_{2u}^{-1}$
$^1T_{2g}$	38.90	31	82	46% $1t_{2u}^{-2}$, 34% $5t_{1u}^{-1}\ 1t_{2u}^{-1}$
$^1A_{1g}$	38.94	–	83	50% $5t_{1u}^{-2}$, 30% $1t_{2u}^{-2}$
^1E_g	38.98	14	83	41% $5t_{1u}^{-2}$, 39% $1t_{2u}^{-2}$
^1E_u	39.00	16	80	44% $5t_{1u}^{-1}\ 1t_{2g}^{-1}$, 18% $1t_{1g}^{-1}\ 1t_{2u}^{-1}$, 32% $1t_{2u}^{-1}\ 1t_{2g}^{-1}$
$^1T_{2g}$	39.16	35	82	38% $1t_{1g}^{-1}\ 1t_{2g}^{-1}$, 20% $1t_{2u}^{-2}$, 11% $5t_{1u}^{-1}\ 1t_{2u}^{-1}$
$^1T_{2u}$	39.31	18	81	31% $1t_{1g}^{-1}\ 1t_{2u}^{-1}$, 22% $1t_{1g}^{-1}\ 5t_{1u}^{-1}$
$^1T_{1u}$	39.39	25	82	30% $1t_{1g}^{-1}\ 1t_{2u}^{-1}$, 20% $1t_{1g}^{-1}\ 5t_{1u}^{-1}$, 11% $1t_{2u}^{-1}\ 1t_{2g}^{-1}$
$^1A_{2u}$	39.47	–	80	56% $1t_{1g}^{-1}\ 1t_{2u}^{-1}$, 23% $5t_{1u}^{-1}\ 1t_{2g}^{-1}$
$^1T_{1g}$	39.49	25	82	55% $1t_{1g}^{-1}\ 3e_g^{-1}$, 23% $5t_{1u}^{-1}\ 1t_{2u}^{-1}$
$^1T_{2u}$	40.17	11	82	60% $1t_{2u}^{-1}\ 3e_g^{-1}$, 22% $5t_{1g}^{-1}\ 3e_g^{-1}$
$^1T_{1g}$	40.55	19	82	81% $1t_{1g}^{-1}\ 1t_{2g}^{-1}$
$^1T_{1u}$	40.67	79	82	41% $5t_{1u}^{-1}\ 3e_g^{-1}$, 32% $1t_{2u}^{-1}\ 3e_g^{-1}$
$^1T_{2g}$	40.80	53	81	42% $1t_{1g}^{-1}\ 3e_g^{-1}$, 14% $5t_{1u}^{-2}$
$^1T_{2u}$	41.03	11	82	29% $5t_{1u}^{-1}\ 3e_g^{-1}$, 21% $1t_{2u}^{-1}\ 1t_{2g}^{-1}$, 11% $5t_{1u}^{-1}\ 1t_{2g}^{-1}$, 10% $1t_{2u}^{-1}\ 3e_g^{-1}$
^1E_u	41.21	11	82	64% $5t_{1u}^{-1}\ 1t_{2g}^{-1}$, 16% $1t_{2u}^{-1}\ 1t_{2g}^{-1}$
$^1A_{1u}$	41.26	–	82	78% $1t_{2u}^{-1}\ 1t_{2g}^{-1}$
$^1T_{1u}$	41.29	9	82	28% $1t_{2u}^{-1}\ 1t_{2g}^{-1}$, 20% $5t_{1u}^{-1}\ 3e_g^{-1}$, 16% $5t_{1u}^{-1}\ 1t_{2g}^{-1}$
^1E_g	41.32	18	79	31% $5t_{1u}^{-1}\ 1t_{2u}^{-1}$, 19% $1t_{2g}^{-2}$, 13% $1t_{1g}^{-2}$
$^1A_{1g}$	41.61	–	81	24% $1t_{2u}^{-2}$, 21% $1t_{2g}^{-2}$, 12% $5t_{1u}^{-2}$, 11% $1t_{1g}^{-2}$, 10% $3e_g^{-2}$
$^1T_{2u}$	42.09	7	81	36% $5t_{1u}^{-1}\ 1t_{2g}^{-1}$, 15% $5t_{1u}^{-1}\ 3e_g^{-1}$, 15% $1t_{2u}^{-1}\ 1t_{2g}^{-1}$
$^1T_{1u}$	42.30	3	81	28% $5t_{1u}^{-1}\ 1t_{2g}^{-1}$, 18% $1t_{1g}^{-1}\ 4t_{1u}^{-1}$, 13% $1t_{2u}^{-1}\ 3e_g^{-1}$, 10% $5t_{1u}^{-1}\ 3e_g^{-1}$
^1E_g	42.33	152	83	67% $3e_g^{-2}$
$^1T_{2g}$	42.68	33	78	28% $1t_{1g}^{-1}\ 1t_{2g}^{-1}$, 20% $1t_{2g}^{-2}$
$^1T_{1g}$	43.20	16	82	58% $3e_g^{-1}\ 1t_{2g}^{-1}$
$^1A_{1g}$	43.21	–	83	42% $3e_g^{-2}$, 23% $5t_{1u}^{-1}\ 4t_{1u}^{-1}$, 15% $1t_{2g}^{-2}$
$^1T_{2g}$	43.28	15	82	59% $3e_g^{-1}\ 1t_{2g}^{-1}$
^1E_u	43.38	36	81	61% $1t_{1g}^{-1}\ 4t_{1u}^{-1}$, 15% $1t_{2u}^{-1}\ 1t_{2g}^{-1}$
$^1A_{1u}$	43.66	–	82	79% $1t_{1g}^{-1}\ 4t_{1u}^{-1}$
$^1A_{2g}$	43.79	–	81	43% $1t_{2u}^{-1}\ 4t_{1u}^{-1}$, 20% $1t_{1g}^{-1}\ 1t_{2g}^{-1}$, 16% $5t_{1u}^{-1}\ 1t_{2u}^{-1}$
$^1T_{2u}$	44.22	22	79	36% $1t_{1g}^{-1}\ 4t_{1u}^{-1}$, 15% $1t_{2u}^{-1}\ 1t_{2g}^{-1}$
^1E_g	44.34	33	80	46% $1t_{2u}^{-1}\ 4t_{1u}^{-1}$, 10% $1t_{1g}^{-1}\ 1t_{2g}^{-1}$
$^1T_{2g}$	44.49	4	81	33% $5t_{1u}^{-1}\ 4t_{1u}^{-1}$, 31% $1t_{2g}^{-2}$, 14% $1t_{2u}^{-1}\ 4t_{1u}^{-1}$
$^1T_{1u}$	44.66	28	79	32% $1t_{1g}^{-1}\ 4t_{1u}^{-1}$, 12% $1t_{2u}^{-1}\ 1t_{2g}^{-1}$
$^1A_{2u}$	44.87	–	72	49% $5t_{1u}^{-1}\ 1t_{2g}^{-1}$, 14% $1t_{2u}^{-1}\ 1t_{2g}^{-1}$
$^1T_{1g}$	44.92	10	79	46% $1t_{2u}^{-1}\ 4t_{1u}^{-1}$, 34% $5t_{1u}^{-1}\ 4t_{1u}^{-1}$
^1E_g	44.92	18	79	26% $5t_{1u}^{-1}\ 4t_{1u}^{-1}$, 15% $1t_{2g}^{-2}$
$^1T_{2u}$	46.00	73	79	51% $3e_g^{-1}\ 1t_{1u}^{-1}$
^1E_u	46.04	45	70	25% $1t_{2u}^{-1}\ 1t_{2g}^{-1}$, 16% $1t_{2g}^{-1}\ 4t_{1u}^{-1}$, 12% $1t_{1g}^{-1}\ 4t_{1u}^{-1}$
$^1A_{1g}$	46.36	–	81	27% $5t_{1u}^{-1}\ 4t_{1u}^{-1}$, 22% $3e_g^{-2}$, 17% $4t_{1u}^{-2}$
$^1T_{2g}$	46.89	40	71	31% $5t_{1u}^{-1}\ 4t_{1u}^{-1}$, 19% $4t_{2g}^{-2}$
$^1A_{2g}$	47.07	–	67	36% $1t_{2u}^{-1}\ 4t_{1u}^{-1}$, 23% $1t_{1g}^{-1}\ 1t_{2g}^{-1}$
$^1T_{1g}$	47.16	38	80	40% $1t_{1g}^{-1}\ 5a_{1g}^{-1}$, 14% $5t_{1u}^{-1}\ 4t_{1u}^{-1}$, 12% $3e_g^{-1}\ 1t_{2g}^{-1}$, 11% $1t_{2u}^{-1}\ 4t_{1u}^{-1}$
$^1T_{2u}$	47.26	26	72	21% $3e_g^{-1}\ 4t_{1u}^{-1}$, 17% $1t_{1g}^{-1}\ 4t_{1u}^{-1}$, 10% $5t_{1u}^{-1}\ 1t_{2g}^{-1}$

(*continued*)

Table 2 (*continued*)

Term	DIE/eV	ΔE/meV	Main/%	Leading configuration weights
$^1T_{2g}$	47.50	42	73	42% $1t_{2u}^{-1}\ 4t_{1u}^{-1}$
^1E_g	47.55	33	69	25% $5t_{1u}^{-1}\ 4t_{1u}^{-1}$, 21% $1t_{2g}^{-2}$
$^1T_{1u}$	47.74	26	71	19% $1t_{1g}^{-1}\ 4t_{1u}^{-1}$, 15% $5t_{1u}^{-1}\ 1t_{2g}^{-1}$, 11% $1t_{2u}^{-1}\ 1t_{2g}^{-1}$
^1E_u	47.95	19	76	67% $1t_{2g}^{-1}\ 4t_{1u}^{-1}$
^1E_g	48.55	66	66	16% $1t_{2u}^{-1}\ 4t_{1u}^{-1}$, 16% $1t_{2g}^{-2}$, 15% $1t_{1g}^{-1}\ 1t_{2g}^{-1}$
$^1A_{2u}$	48.65	–	73	68% $1t_{2g}^{-1}\ 4t_{1u}^{-1}$
$^1A_{1g}$	48.66	–	66	31% $1t_{2g}^{-2}$, 17% $5t_{1u}^{-1}\ 4t_{1u}^{-1}$
$^1T_{2u}$	48.76	48	78	40% $1t_{2g}^{-1}\ 4t_{1u}^{-1}$, 26% $1t_{2u}^{-1}\ 5a_{1g}^{-1}$
$^1T_{1u}$	48.78	49	78	27% $5t_{1u}^{-1}\ 5a_{1g}^{-1}$, 24% $1t_{2g}^{-1}\ 4t_{1u}^{-1}$, 19% $3e_g^{-1}\ 4t_{1u}^{-1}$
$^1T_{1u}$	50.21	59	75	27% $1t_{2g}^{-1}\ 4t_{1u}^{-1}$, 25% $3e_g^{-1}\ 4t_{1u}^{-1}$
^1E_g	50.57	25	82	42% $4t_{1u}^{-2}$, 39% $3e_g^{-1}\ 5a_{1g}^{-1}$
$^1T_{1g}$	51.08	25	69	37% $1t_{1g}^{-1}\ 5a_{1g}^{-1}$, 12% $5t_{1u}^{-1}\ 4t_{1u}^{-1}$, 10% $1t_{2u}^{-1}\ 4t_{1u}^{-1}$
$^1T_{2g}$	51.26	37	81	42% $4t_{1u}^{-2}$, 15% $1t_{1g}^{-1}\ 5a_{1g}^{-1}$
$^1T_{2g}$	53.79	56	73	56% $1t_{2g}^{-1}\ 5a_{1g}^{-1}$, 11% $4t_{1u}^{-2}$
$^1A_{1g}$	54.15	–	76	56% $4t_{1u}^{-2}$

labour of the disk-diagonalization algorithm used [14] to find the eigenvalues and eigenvectors. The diagonal approximation has therefore been employed in the ADC(2) calculations of the double ionizations of SF_6 described here. Tests of the approximation on a variety of small molecules [15] for which the double-ionization energies had been previously calculated without it, indicated that its introduction resulted in systematic small reductions, typically 0.2 eV, in the double-ionization energies of "main" transitions to dication states with significant $2h$ character, together with insignificant changes to the associated eigenvectors [15]. Its effects on the energies of transitions to satellite dication states with effectively no $2h$ character in contrast can exceed 1 eV [15] but, as such transitions are not anticipated to have significant cross sections in DCT processes [16], that poses no problem in this application. A minor shortcoming of discarding the off-diagonal first-order matrix elements of **C** is that some symmetry breaking is thereby introduced. This is manifest as small separations of the energies of states that transform into different components of a degenerate irreducible representation of the spatial symmetry group of the molecule, which symmetry requires to be degenerate. In practice, these separations have not thus far proved significant; most tabulated here for SF_6 are less than 50 meV. For SF_6, calculation of the lowest few eigenvalues of each very large $\mathbf{K} + \mathbf{C}$ matrix has not been attempted with disk diagonalization. Instead, a new, computationally economical, in-core diagonalization algorithm has been developed [15] that further exploits the structure of each sparse ADC(2) matrix to transform the diagonalization into an interative sequence of diagonalizations of the much smaller $2h$ submatrix, the submatrix being modified in each iteration. It is anticipated that this new method will open up the routine application of the ADC(2) method in the diagonal approximation to a wide range of larger molecules.

The FORTRAN code to set up and diagonalize $\mathbf{K} + \mathbf{C}$ by the new iterative method has been interfaced with the GAUSSIAN molecular orbital program package so as to employ the one- and two-electron matrix elements calculated in a molecular-orbital basis by that package. The calculations for SF_6 were performed using GAUSSIAN 94 [17] on the DEC Alpha8400 "Columbus" server at the CLRC Rutherford-Appleton Laboratory. The O_h geometry for SF_6 had bond length $R(S - F) = 0.157$ nm [18]. A standard 6-311G* [17] triple-ζ basis with polarization functions was used for both sulphur and fluorine [19,20] and the SCF total energy thus calculated was -994.1341309 a.u. Following the initial SCF calculation to obtain the molecular orbitals of the neutral SF_6 molecule (the SCF molecule orbital data are listed in Table 1), the post-SCF propagator calculations were carried out for double ionizations to both singlet and triplet dication states, exploiting both spin symmetry and the largest

Table 3
Double-ionization energies (DIE) to triplet states of SF_6^{2+}, calculated with the ADC(2) propagator method using the "diagonal" approximation described in the text

Term	DIE/eV	ΔE/meV	Main/%	Leading configuration weights
$^3T_{1g}$	36.33	33	82	72% $1t_{1g}^{-2}$
$^3A_{2u}$, ^3E_u	37.01	34	83	41% $1t_{1g}^{-1}\ 1t_{2u}^{-1}$, 40% $1t_{1g}^{-1}\ 5t_{1u}^{-1}$
$^3T_{1u}$, $^3T_{2u}$	37.00	38	82	50% $1t_{1g}^{-1}\ 1t_{2u}^{-1}$, 28% $1t_{1g}^{-1}\ 5t_{1u}^{-1}$
$^3T_{1u}$, $^3T_{2u}$	37.50	35	82	49% $1t_{1g}^{-1}\ 5t_{1u}^{-1}$, 30% $1t_{1g}^{-1}\ 1t_{2u}^{-1}$
$^3A_{1u}$	38.47	–	79	69% $1t_{1g}^{-1}\ 5t_{1u}^{-1}$
$^3T_{1g}$, $^3T_{2g}$	38.49	48	82	59% $5t_{1u}^{-1}\ 1t_{2u}^{-1}$, 36% $1t_{1g}^{-1}\ 3e_g^{-1}$, 13% $5t_{1u}^{-2}$
$^3A_{2g}$, ^3E_g	38.61	32	82	81% $5t_{1u}^{-1}\ 1t_{2u}^{-1}$
$^3T_{1g}$	38.64	24	81	44% $1t_{2u}^{-2}$, 20% $5t_{1u}^{-2}$, 14% $5t_{1u}^{-1}\ 1t_{2u}^{-1}$
^3E_u	38.82	11	79	50% $1t_{1g}^{-1}\ 1t_{2u}^{-1}$, 14% $1t_{1g}^{-1}\ 5t_{1u}^{-1}$
$^3T_{1g}$	38.83	36	81	31% $1t_{1g}^{-1}\ 1t_{2g}^{-1}$, 22% $1t_{2u}^{-2}$, 15% $5t_{1u}^{-1}\ 1t_{2u}^{-1}$
$^3T_{1g}$	39.50	23	81	43% $1t_{1g}^{-1}\ 3e_g^{-1}$, 20% $5t_{1u}^{-2}$, 12% $5t_{1u}^{-1}\ 1t_{2u}^{-1}$
$^3T_{2g}$	39.86	53	81	56% $1t_{1g}^{-1}\ 3e_g^{-1}$, 15% $5t_{1u}^{-1}\ 1t_{2u}^{-1}$
$^3T_{2u}$	39.87	50	82	68% $5t_{1u}^{-1}\ 3e_g^{-1}$, 17% $1t_{2u}^{-1}\ 3e_g^{-1}$
$^3T_{1u}$	39.97	22	82	51% $1t_{2u}^{-1}\ 3e_g^{-1}$, 28% $5t_{1u}^{-1}\ 3e_g^{-1}$
$^3T_{2g}$	40.32	21	81	81% $1t_{1g}^{-1}\ 1t_{2g}^{-1}$
$^3T_{2u}$	40.38	30	82	26% $5t_{1u}^{-1}\ 3e_g^{-1}$, 24% $1t_{2u}^{-1}\ 3e_g^{-1}$, 23% $5t_{1u}^{-1}\ 1t_{2g}^{-1}$
$^3T_{1u}$	40.42	13	82	34% $1t_{2u}^{-1}\ 3e_g^{-1}$, 26% $5t_{1u}^{-1}\ 1t_{2g}^{-1}$, 13% $5t_{1u}^{-1}\ 3e_g^{-1}$
$^3A_{2g}$, ^3E_g	40.53	21	81	81% $1t_{1g}^{-1}\ 1t_{2g}^{-1}$
$^3A_{2u}$	41.01	–	81	76% $5t_{1u}^{-1}\ 1t_{2g}^{-1}$
^3E_u	41.05	11	81	41% $5t_{1u}^{-1}\ 1t_{2g}^{-1}$, 37% $1t_{2u}^{-1}\ 1t_{2g}^{-1}$,
$^3T_{1u}$, $^3T_{2u}$	41.24	53	81	76% $1t_{2u}^{-1}\ 1t_{2g}^{-1}$
$^3A_{2g}$	41.37	–	83	82% $3e_g^{-2}$
$^3T_{1g}$	41.77	49	75	41% $1t_{2u}^{-1}\ 1t_{2g}^{-1}$, 10% $5t_{1u}^{-1}\ 1t_{2u}^{-1}$
$^3T_{2u}$	41.79	4	80	54% $5t_{1u}^{-1}\ 1t_{2g}^{-1}$
$^3T_{1u}$	41.82	11	80	51% $5t_{1u}^{-1}\ 1t_{2g}^{-1}$, 13% $1t_{2u}^{-1}\ 3e_g^{-1}$
$^3T_{2g}$	42.76	55	81	71% $3e_g^{-1}\ 1t_{2g}^{-1}$
$^3A_{1u}$	42.96	–	78	39% $1t_{1g}^{-1}\ 4t_{1u}^{-1}$, 35% $1t_{2u}^{-1}\ 1t_{2g}^{-1}$
^3E_u	43.13	3	76	31% $1t_{1g}^{-1}\ 4t_{1u}^{-1}$, 23% $5t_{1u}^{-1}\ 1t_{2g}^{-1}$, 15% $1t_{2u}^{-1}\ 1t_{2g}^{-1}$
$^3T_{1g}$	43.29	56	81	56% $3e_g^{-1}\ 1t_{2g}^{-1}$, 16% $1t_{2u}^{-1}\ 4t_{1u}^{-1}$
^3E_u	43.88	8	74	45% $1t_{1g}^{-1}\ 4t_{1u}^{-1}$, 17% $5t_{1u}^{-1}\ 1t_{2g}^{-1}$
$^3T_{1g}$	44.27	12	80	43% $1t_{2g}^{-2}$, 10% $5t_{1u}^{-1}\ 1t_{2u}^{-1}$
$^3T_{2u}$	44.28	57	79	63% $1t_{1g}^{-1}\ 4t_{1u}^{-1}$
$^3T_{1u}$	44.39	41	79	61% $1t_{1g}^{-1}\ 4t_{1u}^{-1}$
$^3A_{1u}$	44.66	–	69	39% $1t_{1g}^{-1}\ 4t_{1u}^{-1}$, 27% $1t_{2u}^{-1}\ 1t_{2g}^{-1}$
^3E_g	44.75	18	80	72% $1t_{2u}^{-1}\ 4t_{1u}^{-1}$
$^3T_{2g}$	44.75	9	81	42% $1t_{2u}^{-1}\ 4t_{1u}^{-1}$, 38% $5t_{1u}^{-1}\ 4t_{1u}^{-1}$
$^3A_{1g}$	44.80	–	81	79% $5t_{1u}^{-1}\ 4t_{1u}^{-1}$
$^3A_{2g}$	44.80	–	81	69% $1t_{2u}^{-1}\ 4t_{1u}^{-1}$
^3E_g	44.88	2	81	68% $5t_{1u}^{-1}\ 4t_{1u}^{-1}$, 12% $1t_{2u}^{-1}\ 4t_{1u}^{-1}$
$^3T_{1g}$	45.49	25	73	36% $5t_{1u}^{-1}\ 4t_{1u}^{-1}$, 24% $1t_{2g}^{-2}$
$^3T_{1u}$	45.93	92	82	75% $3e_g^{-1}\ 4t_{1u}^{-1}$
$^3T_{1g}$	46.07	52	76	36% $5t_{1u}^{-1}\ 4t_{1u}^{-1}$, 38% $1t_{2u}^{-1}\ 4t_{1u}^{-1}$, 13% $3e_g^{-1}\ 1t_{2g}^{-1}$
$^3T_{2u}$	46.22	64	81	71% $3e_g^{-1}\ 4t_{1u}^{-1}$
$^3T_{2g}$	46.48	64	73	30% $5t_{1u}^{-1}\ 4t_{1u}^{-1}$, 28% $1t_{2u}^{-1}\ 4t_{1u}^{-1}$
$^3A_{2u}$	47.33	–	80	78% $1t_{2g}^{-1}\ 4t_{1u}^{-1}$
^3E_u	47.74	22	77	75% $1t_{2g}^{-1}\ 4t_{1u}^{-1}$
$^3T_{2u}$	47.97	66	78	54% $1t_{2g}^{-1}\ 4t_{1u}^{-1}$, 17% $1t_{2u}^{-1}\ 5a_{1g}^{-1}$
$^3T_{1u}$	48.04	53	78	57% $1t_{2g}^{-1}\ 4t_{1u}^{-1}$, 13% $5t_{1u}^{-1}\ 5a_{1g}^{-1}$
$^3T_{1g}$	48.86	7	76	63% $1t_{2g}^{-1}\ 5a_{1g}^{-1}$
$^3T_{1u}$	49.99	16	75	62% $5t_{1u}^{-1}\ 5a_{1g}^{-1}$
$^3T_{2u}$	50.22	32	73	59% $1t_{2u}^{-1}\ 5a_{1g}^{-1}$
^3E_g	51.09	12	80	80% $3e_g^{-1}\ 5a_{1g}^{-1}$
$^3T_{1g}$	51.22	39	77	72% $4t_{1u}^{-2}$
$^3T_{2g}$	52.59	1	75	73% $1t_{2g}^{-1}\ 5a_{1g}^{-1}$

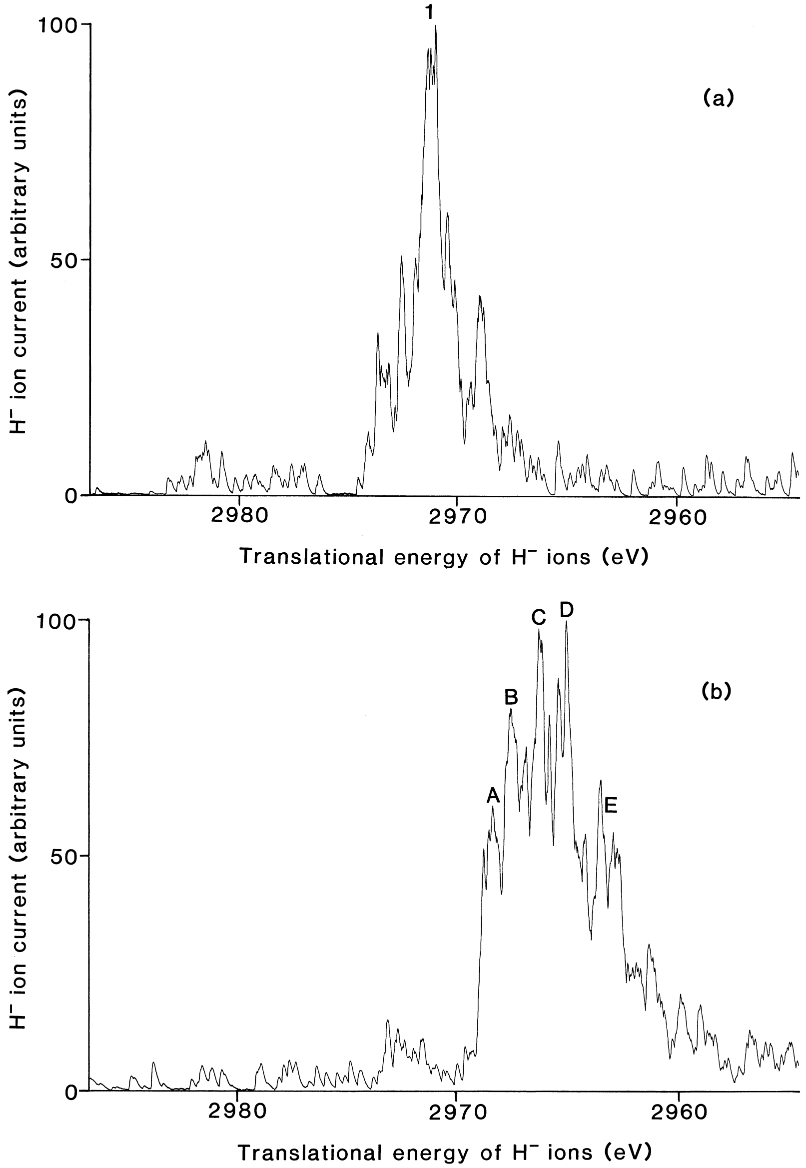

Fig. 1. Typical DCT spectra obtained when H^+ projectile ions interacted with (a) xenon atoms and (b) sulphur hexafluoride molecules.

Abelian subgroup of the symmetry group D_{2h} of the molecule to block diagonalize the ADC(2) matrices. For the 16 blocks, the corresponding irreducible representations of O_h, together with the number of $2h$ configurations and the block dimensions were: ($^1A_{1g}$, $^1A_{2g}$, ^1E_g; 60, 58 812), ($^3A_{1g}$, $^3A_{2g}$, ^3E_g; 36, 83748), ($^1T_{1g}$, $^1T_{2g}$; 32, 56348; repeated twice), ($^3T_{1g}$, $^3T_{2g}$; 32, 81424; repeated twice), ($^1A_{1u}$, $^1A_{2u}$, ^1E_u; 24, 55122), ($^3A_{1u}$, $^3A_{2u}$, ^3E_u; 24, 80256), ($^1T_{1u}$, $^1T_{2u}$; 40, 57574; repeated twice), ($^3T_{1u}$, $^3T_{2u}$; 40, 82592; repeated twice). Eigenvalues in the energy range up to 55 eV for all the blocks were calculated in this work, with their eigenvectors, in order to investigate the importance of the symmetry-breaking effects noted above. The results are given in Tables 2 and 3 where it may be noted that the

Table 4
Comparison of calculated (DIEs) and experimental (DCT) values of double-ionization energies to singlet states of SF_6^{2+}. Closely spaced predictions have been grouped and each group's average DIE, shifted by 2.0 eV (see text), matched with an experimental value

Term	DIE/eV	Group DIE + 2.0 eV	DCT/eV
$^1T_{2g}$	36.59		
^1E_g	36.91	38.9	38.6 ± 0.2
$^1A_{1g}$	36.93		
$^1A_{1u}$, ^1E_u	37.19		
$^1T_{1u}$, $^1T_{2u}$	37.76	39.8	39.7 ± 0.4
$^1T_{2g}$	38.60		
$^1A_{2g}$	38.79		
$^1T_{1g}$	38.80		
^1E_g	38.84		
$^1T_{2g}$	38.90		
$^1A_{1g}$	38.94		
^1E_g	38.98	41.1	40.8 ± 0.3
^1E_u	39.00		
$^1T_{2g}$	39.16		
$^1T_{2u}$	39.31		
$^1T_{1u}$	39.39		
$^1A_{2u}$	39.47		
$^1T_{1g}$	39.49		
$^1T_{2u}$	40.17	42.2	41.9 ± 0.4
$^1T_{1g}$	40.55		
$^1T_{1u}$	40.67		
$^1T_{2g}$	40.80		
$^1T_{2u}$	41.03		
^1E_u	41.21	43.1	43.1 ± 0.4
$^1A_{1u}$	41.26		
$^1T_{1u}$	41.29		
^1E_g	41.32		
$^1A_{1g}$	41.61		

symmetry-breaking energy separations ΔE are not significant in this application. Calculated eigenvectors contained small components of incorrect symmetry due to the symmetry breaking, so the algorithm coded in the computer program for identification of irreducible representations usually failed. In most cases, identification of symmetry type from manual examination of the eigenvector posed no problem, but for a few groups of very closely spaced energy levels, all but two of them triplets, significant mixing of their eigenvectors prevented meaningful symmetry assignments to the individual levels, so entries in the tables for those cases have been grouped and averaged appropriately.

The contents of Tables 2 and 3 indicate, as expected, that the density of electronic states of SF_6^{2+} is very high. For such a large molecule, the lowest double-ionization energy is relatively high and this reflects the exceptionally high binding energies of the occupied molecular orbitals (see Table 1). The unusually large energy difference of ~22 eV between the energies of the highest occupied $1t_{1g}$ and lowest unoccupied $6a_{1g}$ molecular orbitals is reflected by a complete absence of significant mixing of any satellite configurations into the calculated dication states, most of which exhibit main $2h$ character ~80% over the energy range studied. Also in that range, $2h$ configuration interaction is significant in almost all the dication states, as might be expected given the high density of $2h$ configurations of each symmetry.

4. Results and discussion

4.1. Double-ionization energies to singlet electronic states of SF_6^{2+}

The H^+ DCT spectra were obtained in three, nonconsecutive days of experimentation. In all, 20 H^+/SF_6 spectra were recorded, each with its calibration Xe spectrum. A typical spectrum obtained with Xe is shown in Fig. 1(a), and one obtained with SF_6 in Fig. 1(b). It has been shown [21] that the peak marked 1 corresponds to the populating of the $^1D_2$ state of Xe^{2+}. The position of peak 1 was used as E_n(Xe) in Eq. (5) which corresponds to an IE_2(Xe) value of 35.447 eV [11].

It can be seen from Fig. 1(b) that five distinct peaks (marked A–E) are evident. $E_n(SF_6)$ values were determined from their positions, and corresponding $IE_2(SF_6)$ values calculated by inserting these values into Eq. (5). Such data from the 20 spectra recorded have been averaged, and are shown in Table 4 together with the standard deviations in the mean values. Also included in the table are the values calculated for double-ionization energies to singlet states of SF_6^{2+}. These indicate that the density of such states is so high that individual peaks corresponding to transitions to those states would not be resolvable

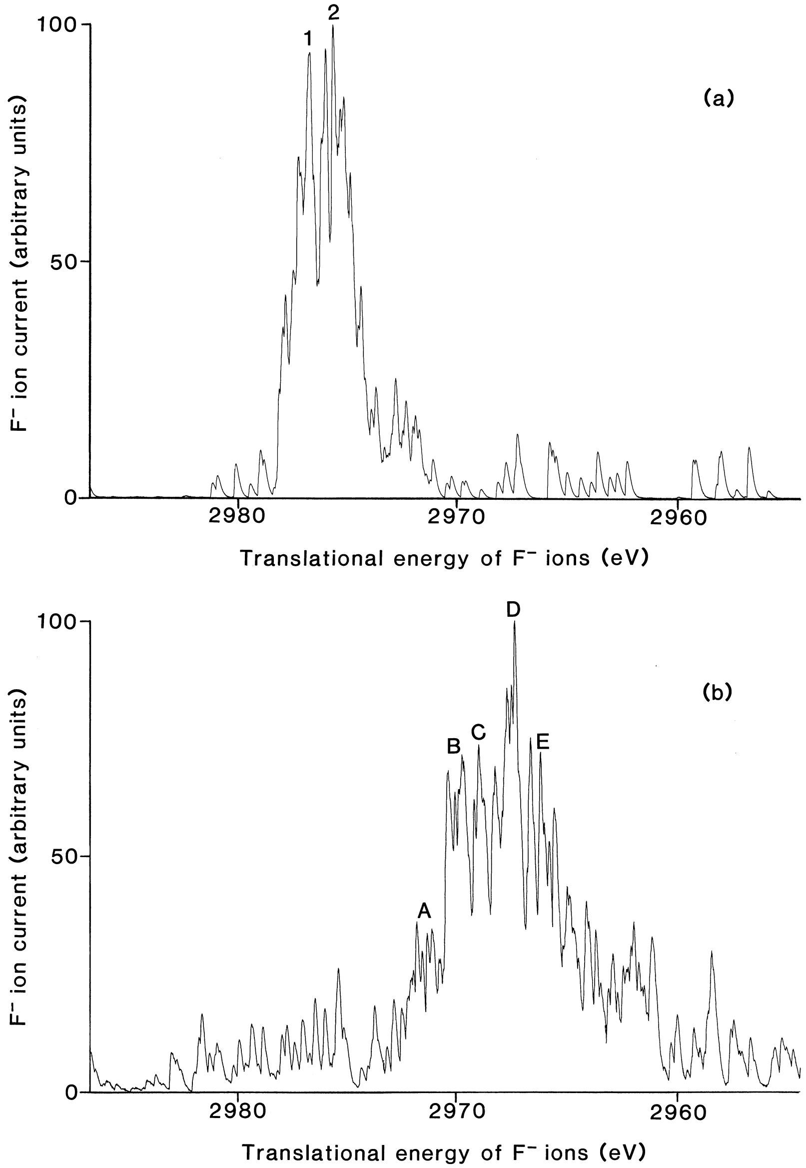

Fig. 2. Typical DCT spectra obtained when F^+ projectile ions interacted with (a) xenon atoms and (b) sulphur hexafluoride molecules.

experimentally. However, as shown in Table 4, it is possible to group together predicted double-ionization energies which are well separated from adjacent groups. To aid comparison of the average values with those measured, 2.0 eV has been added to the average values, giving the values in the third column. It is likely that the ADC(2) approximation is equivalent [12] to a description of the initial and final states to second-order perturbation theory which, for the neutral molecule ground state, usually includes most, but not all, of the contributions to the correlation energy. As a consequence, the energy of the initial state is implicitly predicted to be somewhat higher than is actually the case. The effects on the excited states are much more random, so a systematic small reduction in the predicted transition energies is introduced by the ADC(2) approximation which, as has proven to be the case in many applications, can be corrected for by the addition of a uniform shift to each theoretical value to compensate for any error in the initial state energy.

It can be seen from Table 4 that the calculated values in the third column are in good agreement with the average measured values from the 20 H^+/SF_6 spectra.

4.2. Double-ionization energies to triplet electronic states of SF_6^{2+}

Typical DCT spectra obtained using the F^+ projectile ion are shown in (a) and (b) of Fig. 2. The two peaks in spectrum (a) correspond to the populating of the $^3P_2$ state of Xe^{2+} (peak 1) and/or the $^3P_0$ and $^3P_1$ states (peak 2) which are within 0.3 eV of one another. Because the double-ionization energies to these states are known [11], the positions E_n(Xe) of either peak 1 or 2 can be used in Eq. (5). Five peaks marked A–E were evident in the 24 SF_6 spectra recorded over four nonconsecutive days of experimentation. Their positions give the $E_n(SF_6)$ values which, when inserted into Eq. (5), allow the $IE_2(SF_6)$ values to triplet states of SF_6^{2+} to be calculated. The mean energies, together with the standard deviations, are listed in Table 5. Also included in the table are the double-ionization energies to triplet states of SF_6^{2+} calculated using the computational method described in Sec. 3. The predicted density of states is high but, as for the singlet states, it is possible to establish groups of close-lying double-ionization energies that have relatively large separations from adjacent groups. The average values for such groups, to which 2.0 eV has been added, are shown in the third column of Table 5. It can be seen from the table that those values are in good agreement with the experimental values determined from the 24 F^+/SF_6 spectra.

Table 5
Comparison of calculated (DIEs) and experimental (DCT) values of double-ionization energies to triplet states of SF_6^{2+}. Closely spaced predictions have been grouped and each group's average DIE, shifted by 2.0 eV (see text), matched with an experimental value

Term	DIE/eV	Group DIE + 2.0 eV	DCT/eV
$^3T_{1g}$	36.33	38.3	38.2 ± 0.5
$^3A_{2u}$, ^3E_u	37.01	39.2	39.6 ± 0.3
$^3T_{1u}$, $^3T_{2u}$	37.00		
$^3T_{1u}$, $^3T_{2u}$	37.50		
$^3A_{1u}$	38.47	40.6	40.9 ± 0.3
$^3T_{1g}$, $^3T_{2g}$	38.49		
$^3A_{2g}$, ^3E_g	38.61		
$^3T_{1g}$	38.64		
^3E_u	38.82		
$^3T_{1g}$	38.83		
$^3T_{1g}$	39.50	42.1	42.3 ± 0.4
$^3T_{2g}$	39.86		
$^3T_{2u}$	39.87		
$^3T_{1u}$	39.97		
$^3T_{2g}$	40.32		
$^3T_{2u}$	40.38		
$^3T_{1u}$	40.42		
$^3A_{2g}$, ^3E_g	40.53		
$^3A_{2u}$	41.01	43.4	43.6 ± 0.4
^3E_u	41.05		
$^3T_{1u}$, $^3T_{2u}$	41.24		
$^3A_{2g}$	41.37		
$^3T_{1g}$	41.77		
$^3T_{2u}$	41.79		
$^3T_{1u}$	41.82		

5. Conclusions

The results of the investigation reported in this article have considerably enhanced our knowledge of the double ionization of SF_6. The calculated double-ionization energies show that the densities of both singlet and triplet states of SF_6^{2+} are high. The resolving power of the DCT spectrometer used in the experimental part of the study was not high enough to show peaks due to transitions to each state. It is possible, however, to establish groups of states corresponding to close-lying calculated double-ionization energies for which the upper and lower values are well separated from the corresponding values of adjacent groups. When the average double-ionization energies of these groups were compared with the results measured from the recorded DCT spectra, good agreement was evident. This confirms that the computed data reflect accurately the double-ionization energies to singlet and triplet electronic states of SF_6^{2+}.

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