Momentum-transfer dependence of S 2p excitations of sulfur hexafluoride by angle-resolved electron-energy-loss spectroscopy

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Absolute generalized oscillator strengths (GOS's) of S 2p excitations of SF_6 have been determined as a function of momentum transfer K, using angle-resolved electron-energy-loss spectroscopy at 2.5-keV impact energy. The GOS for the dipole-forbidden S $2p \rightarrow 6t_{1u}$ transition was found to be significantly enhanced at large K, in contrast to the generally decreasing trend observed for the dipole-allowed discrete and shape-resonance states of the S 2p shell. A simple empirical analysis based upon the Lassettre series expansion showed that this state has a dominant quadrupole contribution.

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The concept of generalized oscillator strength (GOS) was first introduced by Bethe to describe high-energy inelastic scattering of charged particles [1]. The importance of GOS to the study of electron-impact processes has been reviewed by Inokuti [2]. Lassettre and co-workers have pioneered the use of angle-resolved electron-energy-loss spectroscopy (EELS) for precise GOS measurements and for accurate determination of absolute dipole oscillator strengths (DOS's) by extrapolating the measured GOS data to the dipole limit [3]. The small-angle electron-energy-loss (pseudo-photon) experiments by Van der Wiel, Brion, and co-workers [4] have provided routine measurement of absolute "optical" spectra for photoabsorption and photoionization processes [5]. As well, experiments by Bonham et al. [6] and more recently by Lahmam-Bennani et al. [7] have elucidated important aspects of the complex nature of the high-energy electron-scattering process itself. These K-dependent studies have identified new dipole-forbidden states in the valence shells [8], including the quadrupole transitions in nitrogen [9] and acetylene [10] and octupole transitions in benzene [11] and p-difluorobenzene [12]. While there is a voluminous amount of work on inner-shell dipole excitation [13], only a limited number of variable-angle electron-energy-loss and/or GOS studies have been made in this energy region [14–16].

Recently, there has been considerable interest in the inner-shell excitation of SF_6, with reference to the so-called shape-resonance effect [17]. Numerous experimental studies including both synchrotron-radiation photoabsorption spectroscopy [18,19] and small-angle EELS [20,21] have indicated four bands near the S 2p edge. The two intense bands above the S 2p ionization edge have been identified as shape-resonance states, while a strong discrete state and a weak nondipole band were observed below the S 2p edge [21]. While these experiments have provided important information on the transition energies and absorption cross sections of the inner-shell states, new insights may be obtained if additional parameter(s) appropriate for probing the excitation process can be used. In the present work, we apply angle-resolved electron-energy-loss spectroscopy at 2.5-keV impact energy to investigate inner-shell excitations of the S 2p shell of SF_6. In particular, we provide the first GOS

measurement of inner-shell transitions from the S 2p orbital to the corresponding "virtual" molecular orbitals near the ionization continuum as a function of momentum transfer. It was found that the GOS of the dipole-forbidden S $2p \rightarrow 6t_{1u}$ transition is qualitatively different from those of the dipole-allowed states. We further identify, for the first time, the nature of these inner-shell transitions using a simple analysis of their characteristic GOS's.

A new coplanar $(e,2e)$ spectrometer (operated in the noncoincidence mode) was used to obtain the electron-energy-loss spectrum as a function of the coplanar scattering angle [22]. Briefly, a collimated high-energy electron beam was crossed at right angles with a gas jet expanded from a nozzle (0.5 mm diameter) positioned at 1 cm above the collision center. (The choice of 2.5 keV as the impact energy assured the validity of the first Born approximation.) Electrons scattered with an energy loss at an angle θ from the forward direction were momentum analyzed by one of the two identical secondary electron optical systems. Each of the optical systems consisted of a seven-element lens (with an angular resolution of 0.5° half-angle), a hemispherical energy analyzer (with an energy resolution of 0.6% of the pass energy), and a channel electron multiplier. The electron source and the secondary optical systems were mounted on separate turntables and could be rotated independently. Our spectrometer has an overall energy resolution of 0.8 eV full width at half maximum (FWHM). Sulfur hexafluoride (99.99% purity) was purchased from Matheson and was used without further purification. During an EELS experiment, the ambient pressure of the chamber was maintained at 2×10^{-5} Torr and the pressure at the collision center was estimated to be at least an order of magnitude higher. EELS spectra were also collected at different pressures to assure that multiple-scattering effects were unimportant.

The measured (differential) cross section $d^2\sigma/d\Omega\,dE$ is converted to the (differential) GOS $df(K,E)/dE$ by the Bethe-Born relation [2,6]:

$$\frac{df(K,E)}{dE} = \frac{k_0}{k} K^2 \frac{E}{4} \frac{d^2\sigma}{d\Omega\,dE} , \qquad (1)$$

where $d\Omega$ corresponds to the acceptance solid angle of

the secondary optical system. The square of the momentum transfer ($K = k_0 - k$) can be written as

$$K^2 = k_0^2 + k^2 - 2k_0 k \cos\theta , \qquad (2)$$

where θ is the angle between the momentum vector of the scattered electron k and that of the incident electron k_0. It is important to note that even though our EELS spectra were collected at fixed scattering angles, the change in the momentum transfer with the energy loss can be minimized by using a sufficiently high impact energy. Within the present range of θ, the corresponding momentum transfer is effectively constant at 2.5-keV impact energy over the entire experimental energy-loss range. Finally, the GOS can be made absolute by single-point normalization to absolute photoabsorption data or by using the Bethe sum rule [2,23]:

$$\int \frac{df(K,E)}{dE} dE = N , \qquad (3)$$

where N is the total number of electrons in the target. The Bethe sum rule has been used to obtain absolute GOS data for the valence shell of SF_6 [22]. In this normalization procedure, the intensity of the relative GOS obtained at a particular momentum transfer for the valence shell is numerically integrated over the sampling range, up to 150 eV. The remaining intensity of the valence shell above 150 eV is estimated by fitting a background function $B(E) = a/E^{1.5} + b/E^{2.5} + c/E^{3.5}$ (where a, b, and c are empirical constants) to the Bethe-Born corrected experimental data over the range 60–150 eV [24] and then integrating the function from 150 to 300 eV. The sum of these two integrated intensities is then normalized to the number of valence-shell electrons (after appropriate correction of the contribution due to Pauli excluded transitions from the inner shells). In the case of inner-shell excitations, the same approach of Bethe-sum-rule normalization must be applied with caution. Because of the much weaker cross sections for inner-shell excitations, the constant instrumental background (arising, for instance, from the dark counts of the channeltron) may be sufficiently intense and must be removed before subtraction of the background function $B(E)$. In the present work, we have avoided the Bethe-sum-rule normalization entirely and have chosen to single-point normalize our data to the absolute photoabsorption work of Blechschimdt et al. [18] instead.

Figure 1 shows a series of S $2p$ EELS spectra measured sequentially at three different scattering angles in repetitive scans. These spectra were therefore normalized with respect to one another. Although no attempt was made to put these EELS spectra on an absolute scale, appropriate background functions were subtracted from the Bethe-Born-corrected experimental data. Four absorption bands centered at 173.0, 177.5, 184.5, and 196.3 eV have been previously assigned to transitions from $2t_{1u}$ (S $2p$) to $6a_{1g}$ (band 1), $6t_{1u}$ plus Rydberg states (band 2), $2t_{2g}$ (band 3), and $4e_g$ (band 4), respectively [20,21]. Although each band consists of two-spin-split states in the case of bands 1, 3, and 4, as well as of other states in the case of band 2, only a single Gaussian profile was used to
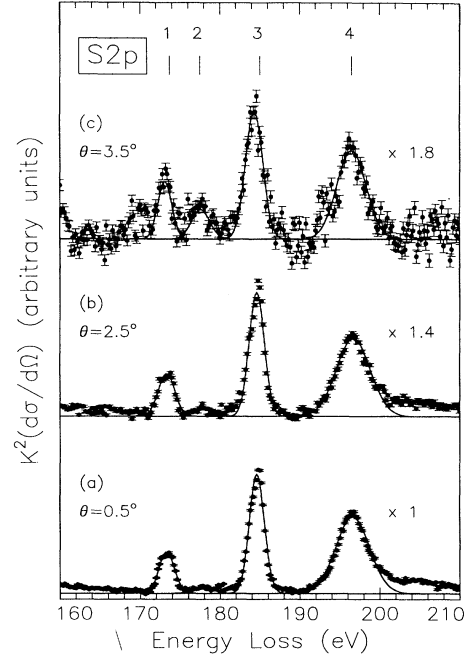

FIG. 1. Angle-resolved electron-energy-loss spectra of the S $2p$ shell of SF_6 at 2.5-keV impact energy and $\theta = 0.5°$ (a), 2.5° (b), and 3.5° (c).

fit each band. The remaining intensity centered at ~ 204 eV [Fig. 1(a)] can be attributed to two-hole–one-particle satellite states [19]. Clearly, with the exception of the S $2p \rightarrow 6t_{1u}$ state (band 2), the other three transitions are dipole allowed. Accordingly, the S $2p \rightarrow 6t_{1u}$ transition should be less intense at $\theta = 0$ (the dipole limit) but enhanced at larger θ, in comparison with the three dipole-allowed transitions. While the spectrum becomes generally weaker at larger angle, the relative intensities of the three dipole-allowed bands remain fairly constant with respect to one another. Despite the somewhat poor statistics at larger angle [Fig. 1(c)], the relative intensity of band 2 is seen to be increasing with respect to the three dipole-allowed bands, in good accord with the proposed assignment.

To determine in more detail the K dependence of these states, we repeated the EELS measurement at a series of scattering angles with a larger energy step in order to improve the statistics. Relative GOS's for the above four transitions were then estimated from the corresponding peak intensities in these EELS spectra after the Bethe-Born correction [Eq. (1)] and appropriate background subtraction, as discussed above. Figure 2 depicts the resulting GOS as a function of K^2 for the four transitions. These GOS curves were made absolute by single-point normalization to the absolute DOS value of the S $2p \rightarrow 2t_{2g}$ transition obtained from the photoabsorption work of Blechschimdt et al. [18] [Fig. 2(c)].

The qualitative difference between the S $2p \rightarrow 6t_{1u}$ transition and the other dipole-allowed transitions is clearly evident in the K dependence of the GOS measurements (Fig. 2). In particular, while the GOS's of the dipole-allowed transitions all decrease in an exponential-
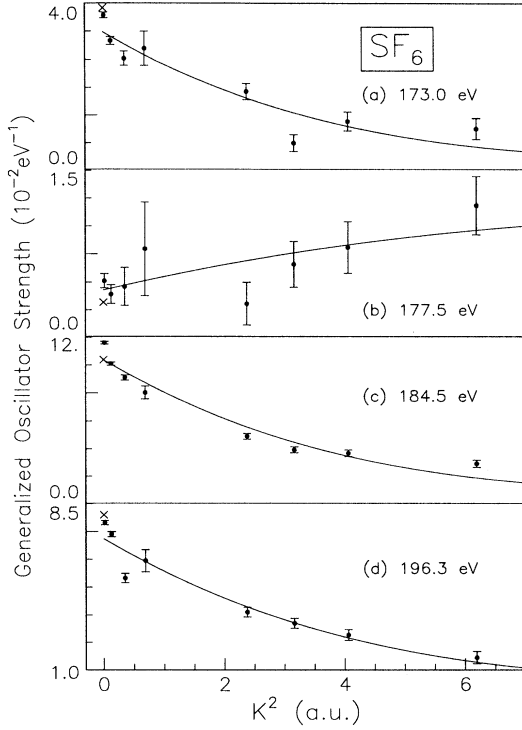
FIG. 2. Absolute generalized oscillator strengths (GOS's) as functions of momentum-transfer squared (K^2) for the S 2p excitations of SF_6 at 2.5-keV impact energy: (a) $2t_{1u}$(S 2p)$\rightarrow 6a_{1g}$, (b) $2t_{1u} \rightarrow 6t_{1u}$ plus Rydberg states, (c) $2t_{1u} \rightarrow 2t_{2g}$, and (d) $2t_{1u} \rightarrow 4e_g$. The GOS's are fitted with empirical functions (solid lines) given by the truncated Lassettre series with f_n parameters indicated in Table I. The GOS curves have been normalized to absolute dipole oscillator strength data [18] (represented by crosses, ×) for the 184.5-eV transition (c).

like fashion with K^2, an increase in the GOS with K^2 is observed for the multipole transition, band 2. This band has been previously assigned in the small-angle EELS work by Brion and co-workers to electron transitions from the S 2p (or $2t_{1u}$) orbital to the $6t_{1u}$ orbital and a series of Rydberg orbitals [20,21]. The observation of dipole-forbidden transitions in their work came about as a result of the finite (albeit very small) acceptance angle of an EELS spectrometer. It should also be noted that "true" dipole limit cannot be reached in practice for "inelastic" electron-impact processes even at zero angle [7]. Because of our limited energy resolution, the GOS of band 2 (i.e., at ~ 177.5 eV) likely includes contributions from the S $2p \rightarrow 6t_{1u}$ transitions as well as all the neighboring unresolved Rydberg transitions. As such, detailed characterization of the nature of these two kinds of states (i.e., S $2p \rightarrow 6t_{1u}$ versus Rydberg) is not possible without improving our energy resolution. While earlier GOS measurements of Rydberg transitions in the valence region have revealed the presence of extrema below $K = 1$ a.u. [25], our present data do not give conclusive evidence for or against any such extrema.

While detailed *ab initio* computations of the GOS are required for a quantitative analysis, some interpretation of the observed difference in the K dependence of the

GOS for the four transitions is in order. Following Lassettre and co-workers, we have fitted the GOS curves (Fig. 2) using a modified form of the so-called Lassettre series [3]:

$$f(K,E) = \frac{1}{(1+x)^6} f_0 \sum_{n=0}^{m} \frac{f_n}{f_0} \left[\frac{x}{1+x} \right]^0, \qquad (4)$$

where $x = K^2 / [(2I)^{1/2} + (2|I - W|)^{1/2}]^2$. I is the ionization potential (i.e., that of S 2p) and W is the excitation energy of a particular discrete transition. Although theoretical extension of the original series to continuum transitions has been made by Dillon, Inokuti, and Wang [26], the strong shape-resonance transitions found above the S 2p edge, which are more discrete-state-like, favor the use of the Lassettre series with two modifications. In particular, the original expression for x has been modified slightly such that the absolute value of the term value (i.e., $I - W$) is used to avoid an imaginary result due to the square root. Furthermore, because of the limited range in K, we have restricted the number of terms in the summation in Eq. (4) to four (i.e., $m = 3$). It was found that if higher-order terms (i.e., $n > 3$) were included, the errors in these terms become extremely large, rendering the corresponding f_n values unreliable. The present truncation of the series to $m = 3$ does not affect the essence of our simple analysis. The f_n values of our truncated Lassettre series are given in Table I.

It is possible to characterize the nature of a particular excitation by comparing the relative magnitudes of the f_n values under appropriate conditions. For instance, in the limit when K approaches zero, $f(K,E)$ approaches the DOS value, f_0. The original Lassettre series was used by Lassettre and co-workers to quantitatively deduce precise DOS values by extrapolating the measured GOS data (obtained by angle-resolved EELS) to the zero K limit. This also forms the basic principle of all pseudophoton or small-angle EELS experiments, which provide an effective simulation of photoabsorption experiments in the forward scattering (or dipole-limit) regime [4]. Furthermore, the result obtained in this nonresonant-type experiment can be made absolute using the Thomas-Reiche-Kuhn sum rule (which is effectively the dipole-limit-version of the Bethe sum rule). Similarly, the second term, f_1, in the series is related to the quadrupole interaction, while the higher-order terms give measures

TABLE I. Values of f_0, f_1, f_2, and f_3 derived from the truncated Lassettre series for the S 2p (or $2t_{1u}$) transitions.

Band no.	Peak maximum (eV)	Assignment $2t_{1u} \rightarrow$	f_0	f_1/f_0	f_2/f_0	f_3/f_0
1	173.0	$6a_{1g}$	0.0327 ±7%	−129.0 ±24%	6108.1 ±48%	−95744.8 ±70%
2	177.5	$6t_{1u}$; plus Rydberg	0.004 21 ±28%	165.3 ±38%	−3784.0 ±46%	20225.8 ±65%
3	184.5	$2t_{2g}$	0.103 ±5%	−124.7 ±15%	5752.4 ±33%	−88964.1 ±49%
4	196.3	$4e_g$	0.0653 ±5%	−123.1 ±18%	5207.6 ±41%	−73127.0 ±67%

of the other multipole contributions. Quantum mechanically, f_n are related to linear combinations of the respective multipole matrix elements. For instance, it has been shown by Huo [27] that the f_1 term is related to the difference of the square of the quadrupole matrix element and the product of dipole and octupole matrix elements. If f_0 (and hence the dipole matrix element) is vanishingly small, a quadrupole transition (i.e., one with a larger quadrupole matrix element) could be characterized by a positive f_1 term. This is in contrast to a dipole transition for which the f_1 term will be negative (i.e., when the product of the dipole and octupole matrix elements is larger and positive). (It is important to note that difficulties may arise if the product of the dipole and octupole matrix elements is negative, in which case a combination of large positive f_1 and small f_0 may also indicate octupole interaction. However, of the limited number of measurements of transitions that have been reported to contain octupole contributions [11,12], we found positive f_0 and negative f_1 in both cases.) The sign alternation between the f_0 and f_1 terms has been observed in earlier molecular GOS studies of valence-shell excitation by Lassettre and co-workers [28] and is clearly evident for the dipole-allowed S $2p$ transitions (1, 3, and 4) in the present study. For the dipole-forbidden S $2p$ transition (2), however, we found that the f_n values are all positive except for f_2. The positive f_1 term, together with the qualitative nature of the plot, therefore provides strong evidence that this state corresponds to a quadrupole transition. Finally, the f_n/f_0 ratios for the dipole-allowed states (1, 3, and 4) are found to be similar in magnitude to one another. The f_n/f_0 ratios for the dipole-forbidden transition (2), on the other hand, are found to be quite different from the corresponding ratios of the dipole-allowed transitions.

The GOS's for dipole-allowed transitions reported in earlier valence-shell molecular GOS studies [28] are found to decrease with K, while those for the nondipole transitions (for instance, the octupole $A\,^1B_{2u} \leftarrow X\,^1A_g$ transitions in benzene [11] and p-difluorobenzene [12]) commonly contain a maximum at some K value (~ 1.0 a.u.). The inner-shell S $2p$ excitations of SF_6 are therefore qualitatively similar to the discrete valence-shell transitions found in other systems. Due to the somewhat coarse angular step employed, the presence of a well-defined maximum in the dipole-forbidden transition cannot be ruled out. The generally increasing trend of the GOS for this state, however, suggests that such a maximum may occur at a higher K value.

In summary, we have provided a GOS measurement of a complete inner-shell (S $2p$) of SF_6 using angle-resolved electron-energy-loss spectroscopy. In particular, qualitative difference in the momentum-transfer dependence of the GOS has been found for the dipole-forbidden S $2p \rightarrow 6t_{1u}$ state, when compared with the other dipole-allowed below-edge discrete and above-edge shape-resonance states. We have also demonstrated the potential of using (absolute) GOS data to characterize the nature of different inner-shell excitation processes. With further improvement in data quality and instrumental resolution, detailed modeling of the multipole interaction (and the corresponding wave functions involved) may be possible. Theoretical studies of the GOS for inner-shell transitions will clearly be of great interest.

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