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Electron impact core excitation of molecules: non-dipole spectroscopy and generalized oscillator strengths

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Abstract

A status report on the field of non-dipole core excitation electron energy loss spectroscopy is given together with a summary of recent studies of S 2*s* generalized oscillator strengths (GOS) of SF_6 and C 1*s* excitation in isomeric xylenes. © 1998 Elsevier Science B.V.

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1. Introduction

Electron energy-loss spectroscopy (EELS) is a powerful tool for studying inner shell electronic transitions [1]. Although modern soft X-ray monochromators outperform inner shell electron energy loss (ISEELS) systems for high-resolution spectroscopy of gases, there are still many useful roles for ISEELS. Most work in this field has been conducted under conditions of small momentum transfer, which effectively simulates photoabsorption. Such conditions are achieved experimentally by using small scattering angles ($\theta < 2°$) and fast electrons, typically using impact energies of more than five times the excitation energy of the core level transition. As the momentum transfer becomes significant (large θ and/or small impact energy), the probability of non-dipole transitions increases. The ability to study electric dipole forbidden processes represents a distinct advantage of electron energy loss relative to photoabsorption spectroscopy.

There have been relatively few studies of non-dipole excitation. Generalized oscillator strengths for specific core excitation transition in a few small molecules have been calculated [2–4]. Experimentally, GOS studies have been carried out on N_2 [5–9], CO_2 [10–12], SF_6 [13–15] and chlorofluorocarbons [16]. In addition, King and collaborators have studied triplet core excited states of a number of small molecules using large angle near-threshold conditions [17,18]. Recently, our group has begun a systematic program to study non-dipole core excitation spectroscopy [14,19,20] and core level GOS [13,21]. This article summarizes some of our recent studies using the McMaster variable angle high resolution electron spectrometer (McVAHRES) which is a variable impact (200–2000 eV), variable scattering angle (–20 to 85°) spectrometer with energy resolution as good as 0.2 eV in the inner shell regime.

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So far, we have studied spin exchange transitions in hydrocarbons [19], differences in singlet and triplet potential surfaces by vibrationally resolved C 1*s* excitation of CO [20], and high precision measurements of generalized oscillator strength (GOS) curves for S 2*p* excitation in SF_6 [13,14]. In this paper we discuss recent extensions of the GOS studies to the S 2*s* level of SF_6. We also describe studies of isomeric identification of xylenes and dimethyl phthalate compounds using dipole regime ISEELS.

2. Results and discussion

2.1. GOS measurements of SF_6

The core excitation spectroscopy of SF_6 is interesting because it is a prototype of a number of species in which a 'cage' of electronegative atoms surrounds a central atom. The associated potential barrier concentrates oscillator strength into a small number of intense core excitation spectral features. Currently we are extending previous S 2*p* work to a study of GOS in S 2*s* region. Fig. 1 plots spectra recorded under near-dipole and largely non-dipole conditions in the region of S 2*p* and S 2*s* excitation of SF_6. The S 2*s* measurements are challenging since it is a weak signal on a strong background. Fig. 2 displays the background subtracted S 2*s* spectra recorded over a range of momentum transfer conditions. There are large intensity redistributions in the S 2*s* spectra under non-dipole conditions. In particular, the quadrupole S 2*s* to a_{1g}, t_{2g} and e_g excitations increase dramatically relative to the dipole t_{1u} transition (see

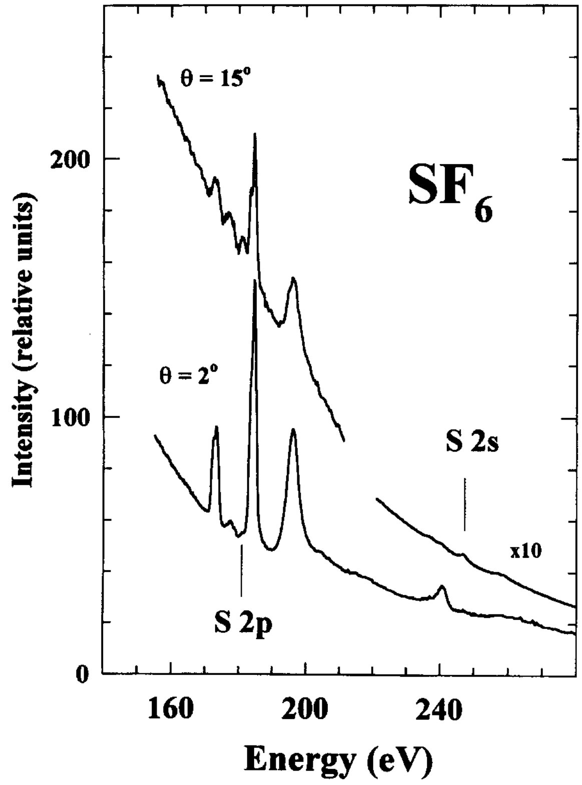

Fig. 1. Electron energy loss spectra (ISEELS) of SF_6 recorded at impact energies (E_o, eV) and scattering angles of (2650, 2°) and (1700, 15°) in the S 2*p* and S 2*s* region. The 15° spectrum has been multiplied by 10 and offset for clarity.

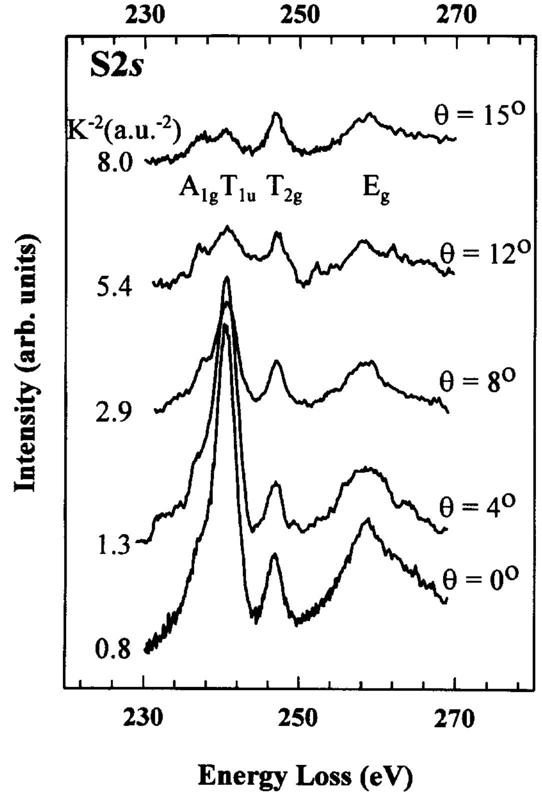

Fig. 2. Background subtracted EELS spectra of SF_6 in the S 2*s* region at the indicated scattering angles and ~1750 eV impact energy (1500 eV + loss). Relative intensities are compensated for gas pressure, beam current and acquisition time. The spectra at 0 and 15° are obtained under different spectrometer conditions and thus there is additional uncertainty in their normalization relative to the 4, 8 and 12° spectra.

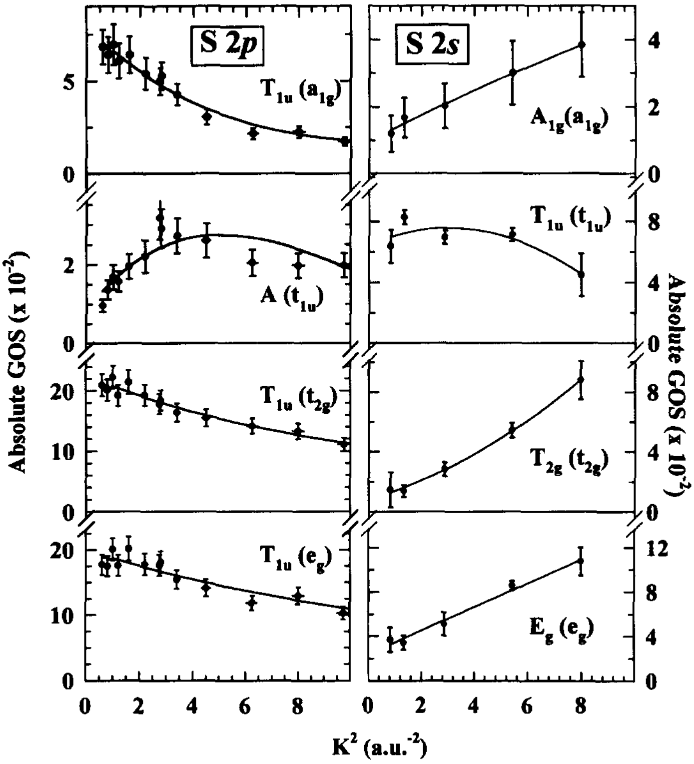

Fig. 3. (Left panel) GOS curves for the $T_{1u}(a_{1g})$, $A(t_{1u})$, $T_{1u}(t_{2g})$ and $T_{1u}(e_g)$ S 2*p* excitations [14]. (Right panel) GOS curves for the $A_{1g}(a_{1g})$, $T_{1u}(t_{1u})$, $T_{2g}(t_{2g})$ and $E_g(e_g)$ S 2*s* excited states derived from the experimental data plotted in Fig. 2.

Ref. [13] for a discussion of the spectroscopy) such that the nondipole signal is more intense than the dipole component above K^2~6 a.u.$^{-2}$.

Generalized oscillator strengths (GOS) [22,23] for the four S 2*s* transitions have been extracted from a quantitative analysis of these spectra. Fig. 3 reports our derived GOS for the four S 2*s* transitions in comparison with those for S 2*p* excitation to the corresponding four upper levels [14]. The measured spectra were normalized to gas pressure, beam current and acquisition time, then converted to relative optical spectra using the Bethe–Born kinematic factors [14,22,23]. The peak areas were evaluated by curve fitting. The relative GOS were converted to an absolute scale by simultaneously measuring the S 2*p* → t_{2g} and S 2*s* → t_{1u} intensities under near-dipole conditions (ratio of peak areas = 0.25(4)) and then normalizing to f_{opt}(S $2p^{-1}$, t_{2g}) = 0.23(2) [14]. At each edge the GOS for dipole-allowed and dipole-forbidden transitions are qualitatively different. That for forbidden transitions tends to zero or a small intensity (related to a vibronically allowed component [13]) at $K^2 = 0$). Our results suggest the GOS for the dipole S 2*p* → a_{1g} and S 2*p* → t_{2g} transitions decays faster than that for the dipole S 2*s* → t_{1u} transition.

2.2. *Isomeric identification by C 1s excitation*

Recently we have investigated the C 1*s* spectra of ortho-, meta- and para- xylenes under dipole scattering conditions to test the sensitivity of core excitation to isomeric identity in disubstituted benzenes [21]. This study was motivated by other recent investigations of the C 1*s* spectra of isomeric dimethyl phthalates [24] and nitroanilines (ortho-, meta- and para-) [25]. In each of these series the shape of the dominant C 1*s* → π* transition was found to depend on the ring-substitution pattern. Fig. 4 compares experimental X-ray absorption spectra [26] with ab initio calculations in the region of the main C 1*s*

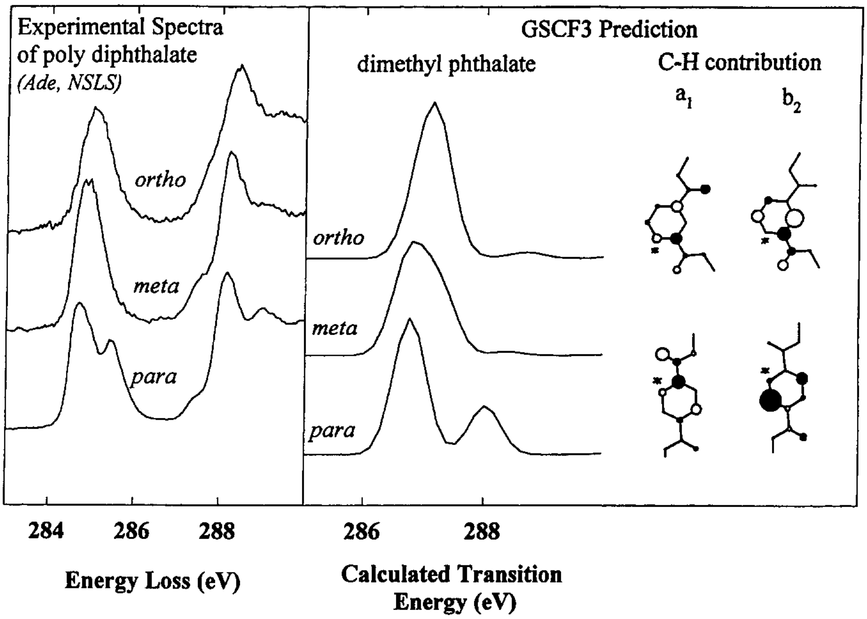

Fig. 4. Comparison of experimental and calculated spectra of dimethyl phthate isomers in the region of the main C 1*s* → π* transition. Molecular orbital pictures are based on the results of ab initio GSCF3 calculations [24].

line. In dimethyl phthalates the lowest energy C 1*s* → π* band in the para- isomer has two components, while the ortho- and meta- isomers exhibit only single peaks. The dimethyl phthalate observations were explained with the help of high level ab initio calculations [26] as arising from isomeric specificity in the intensity of the C 1*s* → π* (a_2) transition (one of two components of the symmetry split π*(e_{1u}) molecular orbital (MO) of benzene) [24]. In the isomeric nitroanilines [25] a similar trend was observed, with the main C 1*s* (π*$_{\mathrm{ring}}$ feature of para-nitroaniline exhibiting a distinct high-energy shoulder which is not present in the other two isomers. Here a more complicated spectral interpretation was required but it also invoked isomeric differences in the symmetry-splitting of the π*(e_{1u}) MO of benzene to explain the isomeric spectral dependence. The goal of the present work was to investigate a system without the complexity of substituent-ring delocalization, which is a major complicating factor in the phthalates and nitroanilines, to see if the isomeric sensitivity was solely of geometric origin.

Fig. 5 plots the ISEELS spectra in the region of the main π* band, along with the results of GSCF3 calculations. The lineshape of the C 1*s* → π* transition in xylenes does depend on the substitution pattern, with *para*-xylene exhibiting two components, *ortho*-xylene a single asymmetric peak, and meta-xylene a single peak. Improved virtual orbital ab initio calculations provide spectral shapes in reasonable agreement with experiment although the calcuated absolute transition energies are about 2 eV too high on account of the limited basis set used. The calculations indicate that the transition responsible for the split π* feature observed in the C 1*s* spectrum of para-xylene is associated with the methyl substituted ring carbons, for which there is a somewhat larger chemical shift in the para- relative to the ortho- or *meta*- isomers. Thus, while a somewhat analogous experimental observation is made, the calculations indicate the origin of the isomeric sensitivity is quite different in the xylenes, as compared with the dimethyl phthalate or nitroanilines. These results will be presented in greater detail elsewhere [21].

3. Conclusions

Even though the potential of EELS to provide spectroscopic information complementary to optical

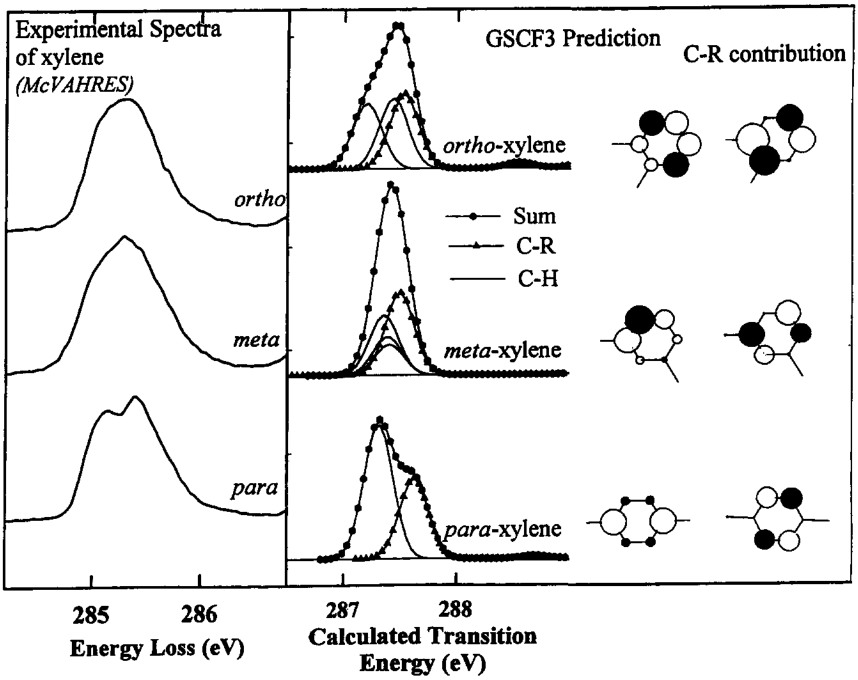

Fig. 5. Comparison of experimental and calculated spectra of xylene isomers in the region of the main C 1s → π* transition. Molecular orbital pictures are based on the results of ab initio GSCF3 calculations.

excitations has been known for years, there has been little examination of non-dipole core excitation spectroscopy and relatively few systematic measurements of GOS spectrometry for inner-shell excitation. The work described herein represents part of a systematic program of studies in this area.

Acknowledgements

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References

[1] A.P. Hitchcock, Physica Scripta T 31 (1990) 159.

[2] T.N. Rescigno, A.E. Orel, J. Chem. Phys. 70 (1979) 3390.

[3] M.P. de Miranda, C.E. Bielschowsky, J. Mol. Struct. 282 (1993) 71.

[4] R.A. Bonham, M. Inokuti, R.S. Barbieri, J. Phys. B 26 (1993) 3363.

[5] R. Camilloni, E. Fainelli, G. Petracelli, G. Stefani, in: EXAFS and Near Edge Structure, Springer, Berlin, 1983, p. 174.

[6] R. Camilloni, E. Fainelli, G. Petracelli, G. Stefani, F. Moracci, R. Platania, Lect. Notes in Chemistry 35 (1984) 172.

[7] R. Camilloni, E. Fainelli, G. Petracelli, G. Stefani, J. Phys. B 20 (1987) 1839.

[8] D.A. Shaw, G.C. King, F.H. Read, D. Cvejanovic, J. Phys. B 15 (1982) 1785.

[9] R.S. Barbieri, R.A. Bonham, Phys. Rev. A 45 (1992) 7929.

[10] D.A. Shaw, G.C. King, F.H. Read, J. Eichler, W. Fritsel, I.V. Hertel, N. Stolterfoht, U. Wille, Proc. 13th ICPEAC, Berlin, 1983, p. 278.

[11] I. Harrison, G.C. King, J. Electron Spectrosc. 43 (1987) 155.

[12] H.M. Boechat-Roberty, C.E. Bielschowsky, G.G.B. De Souza, Phys. Rev. A 44 (1991) 1694.

[13] C.C. Turci, J.T. Francis, T. Tyliszczak, G.G.B. de Souza, A.P. Hitchcock, Phys. Rev. A. 52 (1995) 4678.

[14] J.T. Francis, C.C. Turci, T. Tyliszczak, G.G. B de Souza, N. Kosugi, A.P. Hitchcock, Phys. Rev. A 52 (1995) 4665.

[15] J.F. Ying, C.P. Mathus, K.T. Leung, Phys. Rev. A 47 (1993) R5.

[16] J.F. Ying, K.T. Leung, J. Chem. Phys. 101 (1994) 7311.

[17] I. Harrison, G.C. King, J. Phys. B 19 (1986) L447.

[18] I. Harrison, G.C. King, J. Electron Spectrosc. 43 (1987) 155.

[19] J.T. Francis, C. Enkvist, S. Lunell, A.P. Hitchcock, Can. J. Phys. 72 (1994) 879.

[20] J.T. Francis, N. Kosugi, A.P. Hitchcock,, J. Chem. Phys. 101 (1994) 10429.

[21] I.G. Eustatiu, B. Huo, S.G. Urquhart, A.P. Hitchcock, J. Electron Spectrosc., submitted.

[22] H. Bethe, Ann. Phys. (Leipzig) 5 (1930) 325.

[23] M. Inokuti,, Rev. Mod. Phys. 43 (1971) 297.

[24] S.G. Urquhart, A.P. Hitchcock, A.P. Smith, H. Ade, E.G. Rightor, J. Phys. Chem. B 101 (1997) 2267.

[25] C.C. Turci, S.G. Urquhart, A.P. Hitchcock, Can. J. Chem. 74 (1996) 851.

[26] N. Kosugi, Theor. Chim. Acta 72 (1987) 149.