

An electron energy loss study of the triplet states of SO₂

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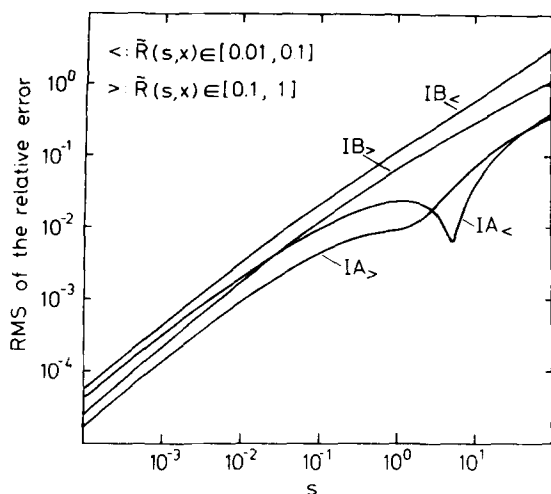


FIG. 2. The rms values of the relative errors of IA and IB as a function of s , for two selected intervals of values of $\tilde{R}(s, x)$.

as IA–IC. The general expression given by Hong and Noolandi⁵ is not included as it is an alternative to a numerical procedure rather than to a closed form expression; the derived small s approximation⁵ is identical with III (or IC).

Figure 1 illustrates the typical behavior of the errors of the various approximate expressions as a function of the exact value of $\tilde{R}(s, x)$. The exact values were calculated by a numerical method⁶ with a controllable accuracy, and the estimated numerical error was always kept smaller than 10^{-6} . For $s \leq 10^{-1}$ useful results may be obtained by IA, IB, or a combination of III(IC) and IV. For $s > 10^{-1}$ only IA can be used.

The s dependence of the accuracy of IA and IB is shown in Fig. 2, which displays the root mean square (rms) values of relative error, estimated over 10 points equidistant in

$\tilde{R}(s, x)$ in the intervals $[0.1, 1.0]$ and $[0.01, 0.1]$, indicated by $>$ and $<$ respectively.

We have also tested the accuracy of the applicable expressions (i.e., IA, IB, IC, and II) for a Coulomb potential and a finite reaction distance x' . We found that varying the reaction distance leads to very small changes in the obtained accuracy, and Figs. 1 and 2 are thus representative of this situation too. This is perhaps not surprising since from an expression valid for $x' = 0$, $\tilde{R}(s, x)_0$, one can always construct an expression valid for $x' \neq 0$ as $\tilde{R}(s, x)_0 / \tilde{R}(s, x')_0$, and the tested expressions either have this form or approximate it when $x' \ll 1$.

Note added in proof: If Euler's constant γ is replaced by $-\gamma$ in IV, as recently suggested,⁷ then an accuracy very similar to IA is obtained for $\tilde{R}(s, x) < 0.5$ [cf. Fig. 1]. A "corrected" version of IV, [Eq. (49) in Ref. 7] has an accuracy similar to but smaller than that of IV; only for $s < 10^{-2}$ and $x > 5$ is a slightly better accuracy obtained. The error of Eq. (49)⁷ increases much faster than that of IV with decreasing values of x for $x \leq 5$. The "modified uniform" first order approximation of Ref. 7 is useful for $s < 10^{-1}$ and for values of $\tilde{R}(s, x) \gtrsim 10^{-2}$, where the relative error is approximately twice that of IB.

¹J. B. Pedersen and P. Sibani, *J. Chem. Phys.* **75**, 5368 (1981).

²L. Monchick, *J. Chem. Phys.* **24**, 381 (1956).

³(a) A. Mozumder, *J. Chem. Phys.* **55**, 3026 (1971); (b) J. L. Magee and A. B. Tayler, *ibid.* **56**, 3061 (1972).

⁴M. Tachiya, *J. Chem. Phys.* **70**, 238 (1979).

⁵K. M. Hong and J. Noolandi, *J. Chem. Phys.* **68**, 5163 (1978).

⁶J. E. Larsen and J. B. Pedersen (submitted).

⁷S. Raaen and P. C. Hemmer, *J. Chem. Phys.* **76**, 2569 (1982). All terms (rather than just the last) in the first line of Eq. (49) should, according to P. C. Hemmer, be multiplied by $z^{-1}e^{-z}$. In Fig. 1 and Table I $\kappa^2 = 0.01$. The corrected expression (49) was used in the comparison.

An electron energy loss study of the triplet states of SO₂^{a)}

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The location of the low lying triplet states of SO₂ has been the subject of considerable interest: many experimental studies and theoretical calculations have been directed to this end. Theory predicts the existence of two nearly degenerate low lying triplets ³B₁ and ³B₂ at ~2.5 eV,¹ while other calculations place the ³B₂ state at even lower energy 1.3 eV.² Although the theoretical calculations were not optimized to accurately determine excitation energies, the theoretical predictions of nearly degenerate low lying triplets and the possibility of a low energy ³B₂ state have been considered in the discussion

of the photophysics and photochemistry of SO₂.³ Optical spectroscopy has firmly located the ³B₁ state at 3.21 eV.⁴ Other triplet states have been seen only indirectly. For example, by a detailed analysis of the perturbations in the ³B₁ absorption spectrum, the ³A₂ state was placed at 3.23 eV⁵ in the gas phase, while other experiments⁶ suggest that the ³B₁–³A₂ ordering is reversed in the solid. Magnetic field effects⁷ on the singlet absorption spectrum in the 4 eV region also reveal triplet perturbations. Finally, the multiphoton ionization (MPI) spectrum of gas phase SO₂⁸ shows evidence of an-

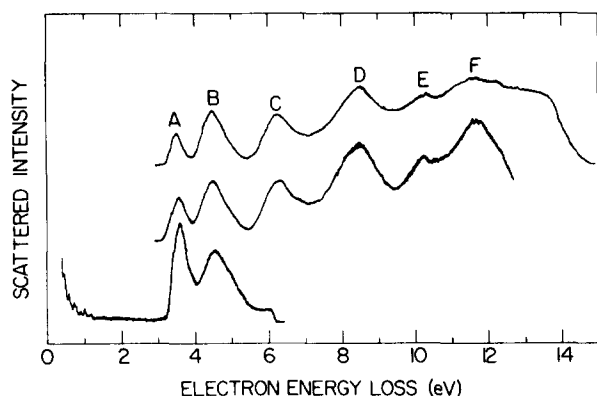


FIG. 1. Electron energy loss spectra of solid SO_2 at 20 K. The energy loss spectra shown were obtained with different electron beam energies, i.e., about 14 (top), 12 (middle), and 6 eV (bottom). The respective peak energies are at A: 3.5 eV, B: 4.5 eV, C: 6.3 eV, D: 8.4 eV, E: 10.2 eV, and F: 11.6 eV.

other excited triplet resonance at either twice or three times the energy of the 3B_1 state.

Electron impact excitation has proven to be an effective tool for locating triplet levels because the spin-forbidden character of the singlet-triplet transitions can be relaxed. Two such studies of SO_2 have already been performed. Foo *et al.*⁹ reported the electron energy loss spectrum (EELS) of gaseous SO_2 in the 3–16 eV range where only singlet valence and Rydberg excitations were detected because of the forward scattering conditions utilized. In the study by Flicker *et al.*,¹⁰ EELS spectrum in the 3–8 eV range showed the expected singlet excitations along with the 3.2 eV triplet.

Here we report our electron energy loss studies of solid SO_2 in the 0–14 eV range which complement these earlier studies. In our study, we have varied the energy of our low energy electron beam so as to observe triplet excitations which become stronger at these low energies due to nondipolar excitation mechanisms. Further the 90° scattering conditions utilized in our measurements will emphasize these forbidden excitations.^{11,12} Also by using solid SO_2 , the Rydberg states are shifted and broadened so that we have the possibility of detecting higher energy triplets.

The EELS spectrometer used in this study has been described in detail elsewhere.¹² The SO_2 was condensed in multilayers on a cold finger at 20 K. The full width at half-maximum of our elastically scattered beam was 15 meV.

In Fig. 1, it can be seen that at low electron beam energies (e.g., 6 eV, bottom curve) the 3.5 eV (vertical) 3B_1 excitation becomes the strongest feature in the loss spectrum. The lack of any electronic excitations at lower energies under these scattering conditions demonstrates that there are no triplet states below 3.5 eV in contrast with the earlier theoretical prediction. Some weak structure can be resolved on the tail of the elastic beam (0 to ~1 eV). The successive peak separation appears to be close to the fundamental frequency

143 meV of the ν_1 mode (sym. stretch) of SO_2 . This structure is therefore due to multiple vibrational excitation (overtones)¹³ and/or multiple electron losses at the fundamental frequency in the bulk material. No vibronic features can be observed in any of the excited states of SO_2 .

As one increases the electron beam energy, higher energy triplets may be observed and become strong at near threshold excitation energies. Three points are noteworthy. First, there is no evidence for a triplet state at twice the energy of the 3.5 eV state. This fact indicates that the structure seen in the MPI experiment⁸ is not due to a two-photon resonance. However, there is a peak at an energy of 10.2 eV which is nearly three times the $^3B_1 - ^1A_1$ energy. This suggests that the 10.2 eV loss corresponds to a triplet state which could also be responsible for the perturbations seen in the MPI spectrum of triplet SO_2 , by acting as a three-photon resonance.

Another feature not common to the gas phase EELS spectrum is seen at 8.4 eV (vertical). This transition may be the same as the 8 eV gas phase loss⁹ which has been shifted in the solid. Alternatively, its high intensity (SO_2 is nearly optically transparent in this region)¹⁴ and the fact that excitations at this energy correlate with overall triplet products,¹⁵ i.e., $\text{SO}(\tilde{X}^3\Sigma^-) + \text{O}(^1D)$, suggest that this loss corresponds to another triplet state. If so, we have detected three of the six expected low lying triplet states of SO_2 (A, D, and E losses in Fig. 1) and have found no evidence for other triplets below 3 eV. The other features in the spectra, B and C are singlet excitations while F is too poorly defined to warrant assignment.

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¹G. L. Bendazzoli and P. Palmieri, *Int. J. Quantum Chem.* **9**, 537 (1975).

²I. H. Hillier and V. R. Saunders, *Mol. Phys.* **22**, 193 (1971).

³K. J. Chung, J. G. Calvert, and J. W. Bottenheim, *Int. J. Chem. Kinet.* **7**, 161 (1975); K. Ahmed, K. F. Langley, and J. P. Simons, *ibid.* **7**, 1659 (1977).

⁴J. C. D. Brand, V. T. Jones, and C. di Lauro, *J. Mol. Spectrosc.* **45**, 404 (1973); K. E. J. Hallin, Y. Hamada, and A. J. Mevev, *Can. J. Phys.* **54**, 2118 (1976).

⁵Y. Hamada and A. J. Mevev (unpublished results).

⁶J. B. Snow, D. C. Hovde, and S. D. Colson, *J. Chem. Phys.* (in press).

⁷J. C. D. Brand, J. L. Hardwick, D. R. Humphrey, Y. Hamada, and A. J. Mevev, *Can. J. Phys.* **54**, 186 (1976).

⁸S. D. Colson, W. Y. Cheung, J. H. Glowinski, and S. J. Riley, *Chem. Phys. Lett.* **76**, 515 (1980).

⁹V. Y. Foo, C. E. Brion, and J. B. Hasted, *Proc. R. Soc. London Ser. A* **322**, 535 (1971).

¹⁰W. M. Flicker, O. A. Mosher, and A. Kuppermann, *J. Chem. Phys.* **69**, 3910 (1978).

¹¹J. P. Doering and J. H. Moore, Jr., *J. Chem. Phys.* **56**, 2176 (1972).

¹²Ph. Avouris and J. E. Demuth, *J. Chem. Phys.* **75**, 4783 (1981).

¹³J. E. Demuth, D. Schmeisser, and Ph. Avouris, *Phys. Rev. Lett.* **47**, 1166 (1981).

¹⁴G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand Reinhold, New York, 1966), Vol. II, p. 512.

¹⁵P. Warneck, F. F. Marmo, and J. O. Sullivan, *J. Chem. Phys.* **40**, 1132 (1964).