

(iii) The line shows the first-order Stark effect which is a characteristic of the Λ -degeneracy. The line resolves into four well-separated components corresponding to $M = \pm 2$ and $M = \pm 1$, as shown in Fig. 1, when an electric field higher than 50 V/cm is applied.

The best signal-to-noise ratio of about 50 was obtained when the partial pressures of OCS and O₂ were 0.085 mm Hg and 0.7 mm Hg, respectively. The analysis of the spectrum for the SO radical in the $^1\Delta$ state is straightforward because the Λ -type doubling in $^1\Delta$ states is very small¹⁷ and both the ³²S and ¹⁶O nuclei have zero spin. Thus the rotational constant for the SO radical in the $^1\Delta$ state is determined to be 21295.1 ± 0.7 MHz and the bond length r_0 to be 1.49198 ± 0.00002 Å. These values agree with the values determined by Brown¹⁶ from the EPR spectrum: $B_0 = 21264 \pm 9$ MHz (0.7093 ± 0.0003 cm⁻¹) and $r_0 = 1.493$ Å.

As mentioned above, the Stark effect for the $J = 3 \leftarrow 2$ transition is of first-order because of the Λ -degeneracy and no magnetic hyperfine interaction. Stark effect measurements were made on four components of the $J = 3 \leftarrow 2$ transition in the electric fields higher than 50 V/cm. The effective distance between the Stark electrodes was calibrated by using the value for the dipole moment of OCS by Muentzer, $\mu = 0.71521 \pm 0.00020$ D.¹⁸ The observed Stark shifts were analyzed by the least-squares method using the following expression $-\mu\Omega M\epsilon/J(J+1)$ for the Stark energy. The dipole moment for the SO radical in the $^1\Delta$ state obtained is 1.336 ± 0.045 D where the uncertainty represents three times the standard error. This value of the dipole moment agrees well with 1.31 ± 0.04 D determined from gas-phase EPR spectroscopy.¹⁹

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stant obtained from the EPR spectroscopy before publication. He is also indebted to Professor Yonezo Morino and Dr. Hiromichi Uehara for helpful suggestions.

¹ F. X. Powell and D. R. Lide, Jr., *J. Chem. Phys.* **41**, 1413 (1964).

² M. Winniewisser, K. V. L. N. Sastry, R. L. Cook, and W. Gordy, *J. Chem. Phys.* **41**, 1687 (1964).

³ T. Amano, E. Hirota, and Y. Morino, *J. Phys. Soc. Japan* **22**, 399 (1967).

⁴ J. E. Solomon, D. R. Johnson, and C. C. Lin, *J. Mol. Spectry.* **27**, 517 (1968).

⁵ C. C. McDonald, *J. Chem. Phys.* **39**, 2587 (1963).

⁶ J. M. Daniels and P. B. Dorain, *J. Chem. Phys.* **45**, 26 (1966); **40**, 1160 (1964); *Bull. Am. Phys. Soc.* **9**, 682 (1964).

⁷ A. Carrington, D. H. Levy, and T. A. Miller, *Proc. Roy. Soc. (London)* **A293**, 108 (1966).

⁸ A. Carrington, D. H. Levy, and T. A. Miller, *Trans. Faraday Soc.* **62**, 2994 (1966).

⁹ A. Carrington, D. H. Levy, and T. A. Miller, *Proc. Roy. Soc. (London)* **A298**, 340 (1967).

¹⁰ A. Carrington, D. H. Levy, and T. A. Miller, *Mol. Phys.* **13**, 401 (1967).

¹¹ A. Carrington, D. H. Levy, and T. A. Miller, *J. Chem. Phys.* **47**, 3801 (1967).

¹² H. Uehara, *Bull. Chem. Soc. Japan* **42**, 886 (1969).

¹³ R. Colin, *Can. J. Phys.* **46**, 1539 (1968).

¹⁴ S. Saito, *Bull. Chem. Soc. Japan* **42**, 667 (1969).

¹⁵ S. Saito and T. Amano, "Microwave Spectrum of the NCO Radical," *J. Mol. Spectry.* (to be published).

¹⁶ J. M. Brown (private communication).

¹⁷ L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Fizmatgiz, Moscow, 1963), p. 373.

¹⁸ J. S. Muentzer, *J. Chem. Phys.* **48**, 4544 (1968).

¹⁹ C. R. Byfleet, A. Carrington, and D. K. Russell (unpublished).

Comments

Comment on "Evaluation of Three-Center Nuclear Attraction Integrals"*

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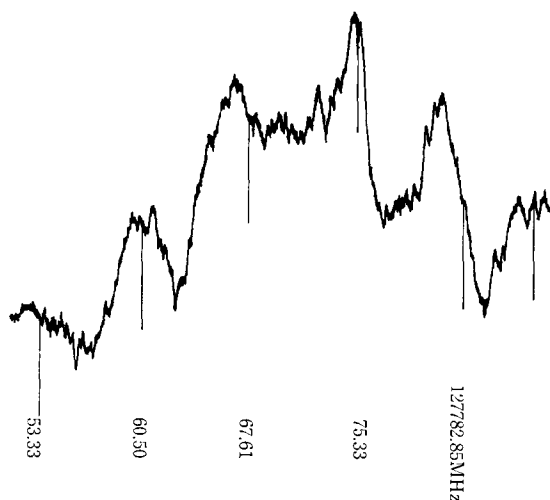


FIG. 1. A recorder tracing of the $J = 3 \leftarrow 2$ transition of the SO radical in the $^1\Delta$ electronic state: Stark dc bias = 55.3 V/cm; Stark ac modulation = 2.3 V/cm; center frequency = 127770.47 MHz.

The simple closed-form expression for three-center nuclear attraction integrals with $1s$ Slater-type orbitals given recently by Kleinman¹ is unfortunately erroneous. Kleinman's formula for the integral [Eq. (33) of Ref. 1] depends explicitly *only* on the *magnitudes* of *two* inter-nuclear distance vectors, but a three-center nuclear attraction integral necessarily depends also on the angle between these vectors.

The major error in the derivation occurs in Eq. (21) of Ref. 1, where, in the integration over θ_2 , the dependence of $1/r_{12}$ on θ_2 has been ignored.

Perhaps it would be possible to carry through Kleinman's approach, which hangs on the solution of the equation,

$$\nabla_2^2 \Phi = \exp(-\gamma r_{2C} - \delta r_{2D}),$$

but the absence of spherical symmetry makes it uncertain that a simple closed-form expression for Φ exists. A standard approach to the solution of such a Poisson equation would be to expand both sides in spherical harmonics, measured say from D . The resulting infinite expansion for the three-center nuclear attraction integral, however, would be equivalent to the expansion obtained directly with the Fourier-transform approach.²

Kleinman's result for two-center nuclear attraction integrals [Eq. (13) of Ref. 1] is correct.

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¹ B. Kleinman, *J. Chem. Phys.* **52**, 1087 (1970).

² H. J. Silverstone, *J. Chem. Phys.* **48**, 4106 (1968).

Errata

Erratum: States of Helium Atoms Adsorbed on Krypton and Xenon Crystals

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Captions to Figs. 9 and 10 should be interchanged; abscissa units in Fig. 10 must be corrected by a factor $\sqrt{2}$ and coordinates in Figs. 11 and 15 by a factor $\frac{1}{2}$.

We are grateful to Dr. F. J. Milford for calling these faults to our attention.