

Erratum: Far Infrared Spectrum of Disiloxane

D. W. Robinson, W. J. Lafferty, J. R. Aronson, J. R. Durig, and R. C. Lord

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⁸ N. Groth and P. Harteck, *Z. Electrochem.* **47**, 167 (1941).

⁹ T. I. Moran and W. W. Watson, *Phys. Rev.* **109**, 1184 (1958).

¹⁰ S. C. Saxena and E. A. Mason, *J. Chem. Phys.* **28**, 625 (1958).

Intermolecular Potential for Krypton

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(Received August 28, 1961)

FENDER¹ has re-examined the experimental data on krypton and reached a more optimistic conclusion than the rather pessimistic one I had suggested earlier.² His conclusion is more palatable on several grounds, and I think he is correct.

The reason for our arriving at different conclusions starting from the same data are rather interesting, and deserve some comment. My basic conclusion can be paraphrased as follows: If one insists on fitting the transport data for krypton (including thermal diffusion) as well as possible, then it is not possible to reproduce the virial coefficients satisfactorily, and *vice versa*; this is not true for helium, neon, argon, and xenon, for which reasonable over-all fits of both transport and virial coefficients are possible. I believe this conclusion remains valid, but different inferences can be drawn from it, which is where Fender and I have differed. My suggestion was essentially that something appeared very peculiar about krypton, which might indicate a lack in our understanding of intermolecular forces. Fender's procedure is to fit the second virial coefficients, accept a small discrepancy of about 2% in calculated viscosities and thermal conductivities, and not worry about a *large* discrepancy in thermal diffusion factors. He then shows that the experimental thermal diffusion factors of all the rare gases are reasonably concordant with each other, although not with the 12-6 potential model. From this point of view the behavior of krypton is not unique.

The main cause of the trouble thus appears to be the thermal diffusion factor α_0 . It has been remarked many times that α_0 is much more sensitive to the intermolecular potential than any other transport coefficient. A small change in the nature of the potential function may well be able to alter α_0 without affecting the other properties appreciably, and so bring about essential agreement. On the basis of Fender's analysis I would therefore suggest that it would be profitable to concentrate largely on thermal diffusion, both experimentally and theoretically.

¹ B. E. F. Fender, *J. Chem. Phys.* **35**, 2243 (1961).

² E. A. Mason, *J. Chem. Phys.* **32**, 1832 (1960).

Erratum: Far Infrared Spectrum of Disiloxane

[*J. Chem. Phys.* **33**, 1004 (1960)]

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THE far infrared spectrum of disiloxane has been reexamined between 30 and 100 cm^{-1} using three different far-infrared spectrometers having spectral slitwidths of the order of 1 cm^{-1} : the instrument¹ on which the compound was originally run,² a vacuum-enclosed Fastie-Ebert spectrometer³ and a Perkin-Elmer model 201C instrument, which is similar in design and performance to the original instrument.⁴ With all three spectrometers the existence of absorption was confirmed, the maximum absorption coefficient at about 68 cm^{-1} having roughly the value originally obtained ($2 \times 10^3 \text{ cm}^2/\text{mol}$). An investigation which started as a search for the next lower maximum has failed, however, to confirm the maxima and minima previously reported,² and we believe that they are spurious.

Study of the original records from which the points shown on the curves in Fig. 1 of reference 2 were obtained clearly indicates these maxima and minima at the pressures used, but we cannot say with certainty what produced them. They were possibly the result of a combination of: (1) slight drift in background between runs; (2) changes in water-vapor concentration in the optical path; and (3) variation in interference fringes in the polyethylene cell windows with pressure. We believe that no one of these factors alone could have

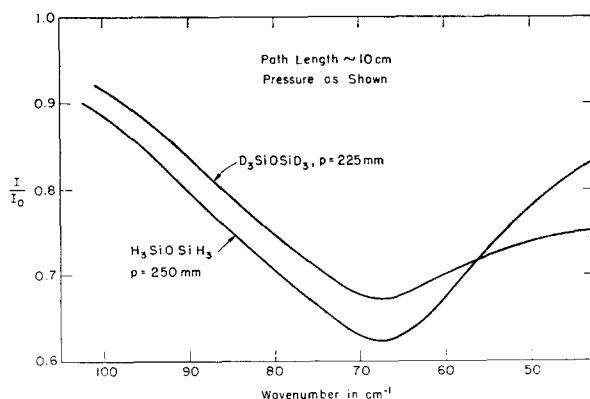


FIG. 1. Far-infrared absorption of disiloxane and disiloxane- d_6 . Spectral slitwidth about 1 cm^{-1} .

produced the maxima and minima under the conditions of the original investigation, but obviously the detailed explanation of this spectral structure put forth by us in the original paper² no longer applies.

The absorption spectrum of the fully deuterium-substituted molecule has now been observed under closely similar conditions to those used in the measurement of the disiloxane spectrum. A broad featureless band occurs with maximum absorption at a position indistinguishable under the conditions of the observations from that of the disiloxane band, and with nearly the same absorptivity. The two bands have closely similar shapes, though the absorption of disiloxane-*d*₆ appears to be somewhat stronger on the low-frequency side. The two band contours are compared in Fig. 1, and show that there is little difference between them, as would be expected if the absorption is due almost entirely to the motion of the oxygen atom.

Although the above results are rather indefinite in their structural implications, the low frequency of the absorption maximum, taken together with the very wide Si—O—Si bond angle (near 150°), does indicate a flat and anharmonic potential function for the bending motion. Thus the motion must be treated with due consideration of the special shape of the potential function characteristic of the quasi-linear molecule, as has been done by Thorson and Nakagawa.⁴ However resolution of the fine structure predicted by them, which our earlier work² seemed to have verified, will apparently require considerably higher resolving power than is presently available to us, and possibly also a study of the molecule at greatly reduced temperatures.

The authors gratefully acknowledge the financial sponsorship by the National Science Foundation at M.I.T. and the Air Force Office of Scientific Research at the Johns Hopkins University.

¹ R. C. Lord and T. K. McCubbin, Jr., *J. Opt. Soc. Am.* **47**, 689 (1957).

² J. R. Aronson, R. C. Lord, and D. W. Robinson, *J. Chem. Phys.* **33**, 1004 (1960).

³ D. W. Robinson, *J. Opt. Soc. Am.* **49**, 966 (1959).

⁴ W. R. Thorson and I. Nakagawa, *J. Chem. Phys.* **33**, 996 (1960).

Erratum: Magnetic Properties and Optical Absorption Spectrum of K₂ReCl₆

[*J. Chem. Phys.* **34**, 1628 (1961)]

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DR. W. A. Runciman has kindly pointed out to me that in Table III the matrix element between the second ²E_g state and the first ⁴T_{1g} state should be $\frac{1}{6}\sqrt{3}\zeta$ instead of $\frac{1}{3}\sqrt{3}\zeta$. This mistake does not appear in the manuscript or the galley proofs; the numerical results of the paper are therefore unaffected.

Erratum: Statistical Mechanics of Isotope Effects on the Thermodynamic Properties of Condensed Systems

[*J. Chem. Phys.* **34**, 1485 (1961)]

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DR. Marvin Stern has kindly called my attention to the following errata in the manuscript:

- (1) Multiply right-hand side of Eq. (3.9) by N^{-1} ;
- (2) Eq. (3.14), replace $(\lambda_{ic}^{0'})^{2j}$ by $(\lambda_{ic}^{0'})^j$;
- (3) Eq. (3.15), replace $(4\pi^2 N)^{-1} \Sigma \nu_{ic}^{0'} (\lambda_{ic}^{0'})^j$ by $N^{-1} \Sigma \nu_{ic}^{0'} (\lambda_{ic}^{0'} / 4\pi^2)^j$;
- (4) Eq. (3.18), write $u_{ib}' > 2\pi$;
- (5) Eqs. (4.21) and (4.22). Each term on the right-hand side should contain the factor $\beta\gamma$.
- (6) In the equation in the middle of page 1492, $\gamma = \alpha V / \beta C_v$, α is used in the conventional manner as the symbol for the coefficient of expansion, and not as the compressibility. The conventional symbol β has already been used for the compressibility;
- (7) Eq. (6.2), replace F by G .

Erratum: Comprehensive Investigation of the Electronic Spectroscopy and Theoretical Treatments of Ferrocene and Nickelocene

[*J. Chem. Phys.* **35**, 516 (1961)]

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THE majority of the following corrections were necessitated by the discovery of an error in group theoretical notation for the $4p_z$ orbital in the D_{5d} point group. This error also occurs in the original references 1, 12, 16, and 17 as well as in other publications.¹ The correct notation for the $4p_z$ orbital in the D_{5d} group is a_{2u} instead of a_{1u} .

In Fig. 5, the $4p(a_{1u})$ levels of Moffitt and of Dunitz and Orgel should read $4p(a_{2u})$. In Figs. 6 and 7, the $\bar{p}(a_{1u})$ level of Liehr and Ballhausen should read $\bar{p}(a_{2u})$.

In Table VII, line 2 should read a_{2u} for a_{1u} under D_{5d} . In Table IX under Moffitt, line 9 should read $4p(a_{2u})$ for $4p(a_{1u})$. In Table IX under Dunitz and Orgel, line 9 should read $4p(a_{2u})$ for $4p(a_{1u})$. In Table X under Dunitz and Orgel, line 2 should read $e_{1g} - 4p(a_{2u})$ for $e_{1g} - 4p(a_{1u})$. Line 9, $[e_{1u} - 4p(a_{1u})]$, should