

Letters to the Editor

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Communications

Evidence for Pseudo-Jahn-Teller Effect in XeF_6^*

L. S. BARTELL

Department of Chemistry, University of Michigan,

Ann Arbor, Michigan

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ENOUGH clues about the unusual molecule XeF_6 have accumulated to warrant a preliminary interpretation of its structure.¹ According to the valence-shell electron-pair repulsion model of Gillespie *et al.*,^{2,3} the molecule should be distorted from O_h symmetry. Despite widespread conjecture to the contrary, the simple Hückel MO model leads quite naturally to similar conclusions.⁴⁻⁷ The most direct experimental evidence obtained so far, perhaps, has been provided by gas-phase electron-diffraction studies. Intensities of scattered electrons show conclusively that XeF_6 molecules are not simple, regular octahedra.⁷⁻¹⁰ The intensities can be accounted for reasonably well in terms of a statically deformed structure. Weighting against this interpretation is the fact that the deformation is curiously small—much smaller than expected from Gillespie's rules³—and of the order of magnitude of the vibrational amplitudes required to fit the intensity data.^{7,10} Since an even better fit can be obtained with a model of dynamic distortion symptomatic of a pseudo-Jahn-Teller interaction,¹¹ such a model appears to give the simplest and most plausible basis for understanding the structure.

Interpreting the electron-diffraction data in this light, we may draw several important inferences: (1) The deformation coordinates associated with the negative quadratic force constant¹¹ are the t_{1u} bending coordinates (which, for sake of brevity here, we identify with the pure bending symmetry coordinates S_{4a} , S_{4b} , and S_{4c}).¹² (2) The minimum in the potential-energy function $V_4(\mathbf{R})$ is at $R_e \approx 1 \text{ \AA}$,¹³ where \mathbf{R} is a vector pointing along the lone-pair axis with components S_{4a} , S_{4b} , and S_{4c} . (3) XeF_6 can invert from one stable configuration to another with an oppositely directed \mathbf{R} vector without the necessity of surmounting or tunneling through the potential maximum at $\mathbf{R} = 0$, owing to the triply degenerate character of the t_{1u} inversion mode. (4) The longer Xe-F bonds tend to be those which are adjacent to the xenon lone pair. (5) The t_{2g} mode is strongly coupled to the t_{1u} bending mode by virtue of the large bending amplitudes.¹⁴ (6) Certain lines of

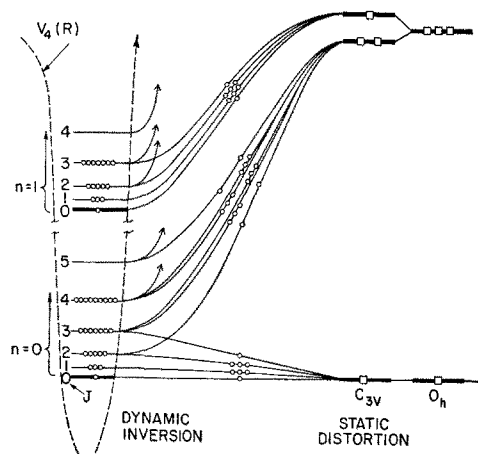


FIG. 1. Schematic correlation diagram for t_{1u} bending vibration levels of a distorted XY_6 molecule. On the left are levels for the "free-rotator" pseudo-Jahn-Teller model. Many quite closely spaced levels with $n > 0$ will exist near this limit irrespective of the depth or shallowness of $V_4(R_e)$ with respect to $V_4(0)$. The progressive splitting of the levels by an increasing octahedral "crystal field" favoring a C_{3v} structure is shown to the limit of a static distortion. The C_{3v} levels are related to those for a normal O_h structure.

evidence suggest that $V_4(\mathbf{R})$ has extrema at C_{4v} and C_{3v} such that a C_{3v} structure is favored.

Conclusions (1) and (4) are also natural consequences of the MO model^{5,7} and consistent with the spirit of Gillespie's model.³ Inference (6) implies that XeF_6 levels fall into groups of inversion octets. Deductions (2) and (3) give us a means of estimating the magnitude of the splitting between the inversion multiplets, as follows.

The proposed t_{1u} inversion potential function $V_4(\mathbf{R})$ exactly parallels that of a rotating diatomic molecule in an octahedral field. If the octahedral field and the not insignificant coupling with t_{1u} stretch coordinates are

neglected, the lowest energy levels should be given approximately by the diatomic formula $J(J+1)\hbar^2/2I_{\text{inv}}$, where J is an inversion quantum number. The "effective moment of inertia," $I_{\text{inv}} \approx (G^{-1})_{44} R_e^2$, is roughly 50-fold smaller than the actual moment of inertia of XeF_6 , according to the diffraction values for R_e and r_{XeF} , implying a frequency of roughly 6 cm^{-1} for the $J=0$ to $J=1$ transition. Therefore, the molecule should show a far-infrared inversion spectrum with rotational structure rather than a microwave spectrum with inversion splitting. The effect of the octahedral field on "free-rotator" levels is illustrated in the correlation diagram of Fig. 1. This diagram suggests that below, say, 200 cm^{-1} the spectrum will consist of many lines, the pattern of which should reveal the location of XeF_6 in the diagram. Furthermore, Conclusion (5) above suggests that the $\Delta J=2$ lines should be strongly Raman active. In addition, combination bands involving the closely spaced inversion levels should give rise to coincidences between the infrared and Raman spectra in the ordinary stretch and bend regions.¹⁵

The above conclusions seem in harmony with the thermodynamic data of Weinstock *et al.*¹⁶ They also appear to be compatible with the recent molecular-beam study by Falconer *et al.*,¹⁷ which proved that the dipole moment of XeF_6 is, at most, a few tenths of a debye. Molecular-orbital calculations indicate that the XeF bonds readjust polarity in t_{1u} deformations so as to repress, in fair measure, the moment produced by displacements of the negative ligands.⁷

A detailed description of experimental results and an extensive discussion of alternative structural models and spectroscopic implications will be forthcoming.^{7,10} Meanwhile, it is hoped that the present Communication will serve to stimulate the spectroscopic research so urgently needed to complete the picture.

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¹ Brevity precludes a discussion of alternative interpretations. It also precludes a resumé of all relevant data.

² N. V. Sidgwick and H. M. Powell, Proc. Roy. Soc. (London) **A176**, 153 (1940); R. J. Gillespie and R. S. Nyholm, Quart. Rev. (London) **11**, 339 (1957). R. J. Gillespie, *Noble Gas Compounds* (University of Chicago Press, Chicago, Ill., 1963), p. 333.

³ R. J. Gillespie, J. Chem. Ed. **40**, 295 (1963).

⁴ L. S. Bartell, Trans. Am. Cryst. Assoc. **2**, 134 (1966); Inorg. Chem. **5**, 1635 (1966).

⁵ B. J. Nicholson (private communication, December, 1966).

⁶ L. Lohr (private communication, January, 1967).

⁷ R. M. Gavin, Jr., and L. S. Bartell (unpublished).

⁸ L. S. Bartell, R. M. Gavin, Jr., H. B. Thompson, and C. L. Chernick, J. Chem. Phys. **43**, 2547 (1965).

⁹ K. Hedberg, S. H. Peterson, R. R. Ryan, and B. Weinstock, J. Chem. Phys. **44**, 1726 (1966).

¹⁰ L. S. Bartell and R. M. Gavin, Jr. (unpublished).

¹¹ U. Öpik and M. H. L. Pryce, Proc. Roy. Soc. (London) **A238**, 425 (1957); D. M. W. Den Boer, P. C. Den Boer, and H. C. Longuet-Higgins, Mol. Phys. **5**, 387 (1962); B. J. Nicholson and H. C. Longuet-Higgins, *ibid.* **9**, 461 (1965). By pseudo-Jahn-Teller effect we imply (following Longuet-Higgins) that in cases where low-lying excited states can mix heavily with the ground state when a distortion occurs, the distortion may become energetically

favorable. For octahedral XeF_6 the ground state is, presumably, A_{1g} and the lowest excited state is T_{1u} . Accordingly, the t_{1u} force constants will tend to be low or, indeed, negative if the interaction is strong enough to qualify as a pseudo-Jahn-Teller interaction. Note that since an analogous destabilization of symmetrical configurations formally applies to all $\text{XY}_m(e_2)_n$ molecules with stereochemically active Gillespie lone pairs, the above definition of pseudo-Jahn-Teller effect is not very restrictive.

¹² For a definition of these coordinates see C. W. F. T. Pistorius, J. Chem. Phys. **29**, 1328 (1958) but note that S_{4d} , S_{5b} , and S_{5c} of the present paper correspond to R_{1b} , R_{2b} , and R_{3b} of Pistorius. For a graphic portrayal of t_{1u} bends leading to C_{2v} and C_{3v} structure, see Ref. 4(a). The fact that the inversion coordinates are not pure bends is strongly indicated by Conclusion (4) of the text and by the abnormally large amplitudes of the XeF bonds.

¹³ This magnitude implies atomic displacements of 0.3 \AA for a pure t_{1u} distortion to C_{3v} symmetry.

¹⁴ The observed correlation between the t_{1u} mode and t_{2g} impurity mode (and to a lesser extent, the e_g impurity mode) is in the direction of relieving the compression between backside ligands when the frontside ligands adjacent to the lone pair are spread apart.

¹⁵ The author is indebted to Dr. H. H. Claassen and Dr. E. L. Gasner for unpublished information on the Raman spectrum showing that the stretching bands actually exhibit coincidences with the infrared (private communication, January 1967, prior to assignment scheme described in text).

¹⁶ B. Weinstock, E. E. Weaver, and C. P. Knop, Inorg. Chem. **5**, 2189 (1966).

¹⁷ W. E. Falconer, A. Buchler, J. L. Stauffer, and W. Klemperer (unpublished).

Observation of the $2p^33s(^5S^0)$ Metastable State of Atomic Oxygen*

GILBERT O. BRINK

Cornell Aeronautical Laboratory, Incorporated, Buffalo, New York

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IN the course of a molecular-beam, magnetic-resonance investigation of the products produced by a microwave discharge in O_2 , a strong resonance was observed in atomic oxygen with a g factor of 2. An examination of the energy levels of atomic oxygen¹ shows that there are only two metastable S states of atomic oxygen, the $2p^4(^1S)$ state that lies 4.2 eV above the ground state and the $2p^33s(^5S^0)$ state that lies at 9.1 eV. Since the 1S state has a zero g factor, the observed resonance must be due to the $^5S^0$ state.

The apparatus used in this work was a conventional

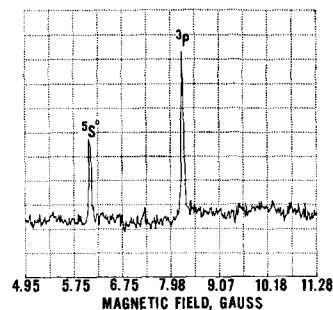


FIG. 1. Zeeman spectrum of atomic oxygen. The rf frequency is 16.800 MHz.