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Author
Schaefer Iii., Henry F.

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Henry F. Schaefer III

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XeF: Chemically Bound?*

Henry F. Schaefer III**

Department of Chemistry and Materials and Molecular Research Division,
Lawrence Berkeley Laboratory, University of California
Berkeley, California 94720

Four years ago, a theoretical study of the $^2\Sigma^+$ and $^2\Pi$ electronic states of XeF was reported.[1] Although the lower $^2\Sigma^+$ potential energy curve was rather flat, there was no other indication of an attraction in excess of the expected Van der Waals. The conclusion drawn in that paper was clearly reflected in its title, "Probable Nonexistence of Xenon Monofluoride as a Chemically Bound Species in the Gas Phase". This was considered a surprising result at the time, since there was general concurrence[2-4] that XeF was a chemically bound species, with dissociation energy $\sim$ 20 kcal/mole.

Despite our theoretical prediction, the assumption of a 20 kcal bond energy has persisted, in particular in this journal. Noteworthy in this regard are the papers by Brau and Ewing[5] (see especially their Figure 10) and by Ault and Andrews.[6]

Very recently this problem has been nicely resolved experimentally by Tellinghuisen and co-workers.[7] They find XeF to have a well depth of $\sim$ 1160 cm^{-1} = 3.3 kcal. Although I am the first to admit that this result makes XeF much more strongly bound than we anticipated,[1] I wish to state here most emphatically my opinion that 3.3 does not a chemical bond make. A better description of the XeF species would be as a charge-transfer complex. Thus, in spite of recent statements to the contrary by Goodman and Brus[8] in this journal, the fundamental conclusion of our study remains correct.

Ultimately, of course, it is not possible to draw a precise distinction between chemical bonds and weaker interactions such as van der Waals forces,[9] hydrogen bonds,[10] and charge-transfer species.[11] As experimental techniques become increasingly sophisticated, bond dissociation energies will almost continuously span the range from 0.02 kcal[12] (He-He) to 256 kcal[13] (CO). Nevertheless it may be pedagogically useful to propose a 10 kcal dissociation energy as a necessary (but not sufficient) requirement for the use of the term "chemically bound". Thus weak chemical bonds, such as the O_2-O bond (24 kcal[14]) in ozone and the FKr-F bond (23 kcal[15]) in krypton difluoride, would be comfortably included.

However, van der Waals molecules would be exluded by this criterion, as would most hydrogen bonds and charge transfer complexes. Obviously there will be ambiguities. For example the $N(CH_3)_3$-SO_2 complex,[16] which is bound by ∿ 10 kcal, should probably not be considered chemically bound. Similarly the Li^+-H_2O and F^--H_2O species,[17] while bound by 35 and 24 kcal, are primarily electrostatic in nature and may not represent true chemical bonds. A third example is the hydrogen bonded HF-H_2O system (∿ 13 kcal),[18] again probably not chemically bound. These examples illustrate clearly that the 10 kcal criterion by no means guarantees that a particular species is chemically bound.

The reader can undoubtedly think of other exceptions[19,20] to this simple rule of thumb. But to stretch the conventional definition of chemical bonding to include the 3.3 kcal XeF is to go beyond reasonable limits.[21]

References

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** John S. Guggenheim Fellow, 1976-1977.

1. D. H. Liskow, H. F. Schaefer, P. S. Bagus, and B. Liu, J. Am. Chem. Soc. 95, 4056 (1973).

2. J. R. Morton and W. E. Falconer, J. Chem. Phys. 39, 420 (1963).

3. H. S. Johnston and R. Woolfolk, J. Chem. Phys. 41, 269 (1964). These authors conclude that XeF is bound by 11 kcal/mole.

4. For a discussion of research on XeF prior to 1972, see N. Bartlett and F. O. Sladky, pages 213-330 of Volume 1, Comprehensive Inorganic Chemistry (Pergamon, Oxford, 1973).

5. C. A. Brau and J. J. Ewing, J. Chem. Phys. 63, 4640 (1975).

6. B. S. Ault and L. Andrews, J. Chem. Phys. 64, 3075 (1976). Although these authors do not mention a specific value of the XeF dissociation energy, they state that their results strongly support the conclusions of Brau and Ewing (reference 5 above), who insist on an XeF bond energy of 10-20 kcal.

7. J. Tellinghuisen, G. C. Tisone, J. M. Hoffman, and A. K. Hays, J. Chem. Phys. 64, 4796 (1976). These authors present a reasonably balanced view of the XeF controversy.

8. J. Goodman and L. E. Brus, J. Chem. Phys. 65, 3808 (1976).

9. S. E. Novick, K. C. Janda, S. L. Holmgren, M. Waldman, and W. Klemperer, J. Chem. Phys. 65, 1114 (1976).

10. M. D. Joesten and L. J. Schaad, Hydrogen Bonding (Dekker, New York, 1974).

11. R. Foster, Molecular Complexes (Elek Science, London, 1973).

12. J. M. Farrar and Y. T. Lee, J. Chem. Phys. 56, 5801 (1972).

13. A. G. Gaydon, Dissociation Energies and Spectra of Diatomic Molecules (Chapman and Hall, London, 1968).

14. G. Herzberg, Spectra of Polyatomic Molecules (Van Nostrand, Princeton N.J., 1966).

15. S. R. Gunn, J. Am. Chem. Soc. 88, 5924 (1966).

16. J. Grundnes and S. D. Christian, J. Am. Chem. Soc. 90, 2239 (1968).

17. H. Kistenmacher, H. Popkie, and E. Clementi, J. Chem. Phys. 59, 5842 (1973); see also W. R. Davidson and P. Kebarle, J. Am. Chem. Soc. 98, 6125 (1976).

18. P. Kollman, J. McKelvey, A. Johansson, and S. Rothenberg, J. Am. Chem. Soc. 97, 955 (1975).

19. A particularly fascinating species we have recently discovered is Li-H_2O, which is bound by ∿ 12 kcal, but shows no electron transfer from Li to H_2O. Although Li-H_2O is a new type of molecular complex, it is debatable whether it should be considered chemically bound. See M. Trenary, H. F. Schaefer, and P. Kollman, J. Am. Chem. Soc. 99, 0000 (1977).

20. It is true, of course, that very strong hydrogen bonds (e.g., FHF^-) and exceptionally strongly bound charge-transfer complexes (e.g., BH_3-NH_3) can reasonably be considered chemically bound. This is especially true when the structures of the separated species are qualitatively altered in the overall complex.

21. Alternative definitions of chemical bonding can be devised on the basis of theoretical considerations, e.g., the importance of overlap and exchange. However, such definitions are usually dependent on imponderables such as basis set size, etc. In addition they tend to

ignore the fact that chemists already have an intuitive feeling for what constitutes a chemical bond. However, it is interesting to note that for the theoretical methods used in reference 1 on XeF do predict chemical bonding for the KrF_2 and XeF_2 species; see P. S. Bagus, B. Liu, D. H. Liskow and H. F. Schaefer, J. Am. Chem. Soc. 97, 7216 (1975).

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TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
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BERKELEY, CALIFORNIA 94720