

NOTES

On the r_0 - and r_e - Structures of H_2O_2

The experimental determination of a r_0 -structure of the H_2O_2 molecule has to cope with the dilemma of extracting four internal parameters out of three rotational B_0 -constants, since no accurate spectroscopic data on D_2O_2 are available. This problem can only be solved by fixing one of the internal parameters in a more or less plausible way. The first r_0 -structure obtained in this way (1) was based on an assumed OH bond length of 95 pm (picometers).¹ Busing and Levy (2) and later Khachkuruzov and Przhevalskii (3) gave convincing evidence that this assumption is not correct: From neutron diffraction results on H_2O_2 (2), D_2O_2 (4), and D_2O (5) as well as from the microwave study of HOF (6) the conclusion can be drawn that an OH bond length of 96 to 97 pm leads to a more reasonable r_0 -structure of H_2O_2 . Similarly, theoretical investigations which include correlation effects suggest a longer OH bond length than 95 pm. An equilibrium value of 96.7(2) pm² has been recently suggested (7).

Certainly, the quantum chemical r_e -parameter does not necessarily present a reliable guess for the corresponding r_0 -value. From spectroscopic investigations on di- and triatomic molecules containing hydrogen it is known (8) that the r_e -value is mostly shorter than the r_0 -value by ca. 1 pm, although exceptions do exist. In order to check whether this is also the case for OH bonds we have calculated the equilibrium structure of H_2O and HOF with Rayleigh-Schrödinger (RS) perturbation theory using the Møller-Plesset (MP) method (9). If the RS-MP approach is applied to the Hartree-Fock wavefunction constructed from a large augmented basis set, electron correlation effects which influence the theoretical r_e -structures are sufficiently handled (7). Employing an augmented [3s2p1d/2s1p] basis (10) the RS-MP method yields for H_2O a $r_e(\text{OH})$ value of 95.7(2) pm and for HOF a value of 97.2(2) pm.³ The observed r_0 -bond lengths are 95.65 (H_2O) (11a) and 96.4(10) pm (HOF) (6). The equilibrium bond length of H_2O has been proposed to be 95.87(1) (11a) and 95.748(2) pm (11b). Hence, the r_0 - and r_e -bond lengths of water are almost identical with a tendency of the equilibrium value to be slightly longer. For HOF the theoretical OH bond is longer by 0.8 pm than $r_0(\text{OH})$. On the other hand, the uncertainty of the experimental value amounts to 1 pm. Furthermore, the remaining HOF parameters which can be determined more precisely by experiment than the OH distance agree well with our RS-MP equilibrium values:

$$r_0(\text{OF}) = 144.2(1) \text{ pm vs } r_e(\text{OF}) = 144.2(2) \text{ pm}$$

and

$$\alpha_0(\text{HOF}) = 97.2(6)^\circ \text{ vs } \alpha_e(\text{HOF}) = 97.0(2)^\circ.$$

Therefore, the correct r_0 -value may be somewhat longer than that given in Ref. (6). We conclude that $r_0(\text{OH}) \leq r_e(\text{OH})$ for the three molecules considered.

In order to determine a reasonable estimate of $r_0(\text{OH})$ for the H_2O_2 molecule we have investigated two recent proposals for the OH bond length which are consistent with our conclusion, namely, $r_0(\text{OH}) = 96.5$ pm suggested by Khachkuruzov and Przhevalskii (3), and $r_0(\text{OH}) = 96.7$ pm suggested by Cremer (7). Using the functional dependencies of $r_0(\text{OO})$, $\alpha_0(\text{OOH})$, and $\theta_0(\text{HOOH})$ on $r_0(\text{OH})$ given by Reddington *et al.* (1), these authors obtained r_0 -structures for H_2O_2 which are considerably outside the margin of error of the values proposed in Ref. (1). As the r_0 -

¹ A r_0 -structure based on an assumed value of $r_0(\text{OH}) = 96.5$ pm is also indicated in Ref. (1).

² Estimated uncertainty on the last digit given in parentheses throughout.

³ The total energies at the computed equilibrium are: $E(\text{H}_2\text{O}) = -76.22245$ and $E(\text{HOF}) = -175.10398$ hartree including correlation energies of -0.19957 and -0.37180 hartree, respectively. The calculated HOH equilibrium angle amounts to $104.1^\circ(2)$.

structure of Ref. (1) was successfully applied to the analysis of the far-infrared spectrum (12) and the millimeter-spectroscopy data (13) of H_2O_2 , the question arises whether the new r_0 -structures are also consistent with these experimental results. To answer this question we have redone the Fourier expansion of the Hamiltonian elements for the semirigid-rotor model of H_2O_2 first given by Hunt *et al.* (12). In this expansion, the dihedral angle θ_0 is the variable and the coefficients are determined from the $r_0(\text{OH})$, $r_0(\text{OO})$, and $\alpha_0(\text{OOH})$ values of Refs. (3) and (7), respectively.

The proper way to determine the dihedral angle is, of course, to set up the Hamiltonian for the semirigid-rotor model (or better, to construct a Hamiltonian that also includes the contributions to the inertial moments from vibrations other than the torsion) and solve for the barrier heights and expectation values of the dihedral angle (or effective moments of inertia), but this is outside the scope of this note. Instead we will simply use the coefficients β , ν , and γ of P'^2 , $P_x'^2$, and $(P_x'^2 - P_y'^2)$ in the semirigid Hamiltonian, and solve for the angle θ_0 by the trigonometric relations.

As was shown by Oelfke and Gordy (13) the mm-experiment yields very accurate values for β , ν , and γ , namely: $\beta = 0.85600(7)$, $\nu = 9.21331(7)$, and $\gamma = -0.01811(2) \text{ cm}^{-1}$ for the lowest state of H_2O_2 . With these constants and the Fourier expansion from Ref. (12), Oelfke and Gordy chose to calculate θ from γ alone (obtaining $\theta_0 = 120.2^\circ$) apparently because the equation from ν yielded $\theta_0 = 124.3^\circ$ and the equation from β was unsolvable.

With the new Fourier expansion (Table I) we obtain for $r_0(\text{OH}) = 96.5 \text{ pm}$ the following values for the dihedral angle θ_0 : 121.6° (from ν) and 120.2° (from γ); for $r_0(\text{OH}) = 96.7 \text{ pm}$: 139.1° (from ν) and 120.0° (from γ), while the equations for β are unsolvable. The spectroscopic constants determine the values of θ_0 to within 0.05° . Model calculations have shown the γ -equation to be stable. The β -equation is numerically very unstable (the difference of two like numbers are divided by a very small number) and the Fourier expansion to $\cos 2\theta_0$ is likely to be inadequate in the ν -equation. From this and the computed dihedral angles we can draw two conclusions: (i) The mm-spectroscopy data support the r_0 -structure proposed by the Russian authors (3). (ii) The γ -equation strengthens the evidence for an θ_0 angle of 120.2° . It should also be mentioned that for the r_0 -structure of Ref. (3) the extrapolation of the curves in Fig. 6 of Ref. (13) makes the apparent difference in the $r_0(\text{OH})$ and $r_0(\text{OD})$ distances shrink from 1 pm to ca. 0.3 pm (to lead to $r_0(\text{OD}) = 96.2 \text{ pm}$) in line with the assumed near-equality of $r_0(\text{OH})$ and $r_e(\text{OH})$.

TABLE I

Fourier Expansion of the Coefficients of the Rigid Rotor Part of the Semirigid Rotor Hamiltonian of Hunt *et al.* (12) Using the Parameters of Refs. (3, 7).

$r_0(\text{OH}) = 96.5 \text{ pm}, r_0(\text{OO}) = 146.4 \text{ pm}, \alpha_0(\text{OOH}) = 99.4^\circ$
$\beta(\theta_0) = 0.858\ 25 + 0.002\ 83 \cos \theta_0 + 0.000\ 867 \cos 2\theta_0$
$\nu(\theta_0) = 9.121\ 13 - 0.186\ 39 \cos \theta_0 + 0.012\ 21 \cos 2\theta_0$
$\gamma(\theta_0) = 0.000\ 587 + 0.037\ 11 \cos \theta_0 + 0.000\ 062 \cos 2\theta_0$
$r_0(\text{OH}) = 96.7 \text{ pm}, r_0(\text{OO}) = 146.3 \text{ pm}, \alpha_0(\text{OOH}) = 99.3^\circ$
$\beta(\theta_0) = 0.859\ 38 + 0.002\ 85 \cos \theta_0 + 0.000\ 879 \cos 2\theta_0$
$\nu(\theta_0) = 9.072\ 05 - 0.184\ 55 \cos \theta_0 + 0.012\ 17 \cos 2\theta_0$
$\gamma(\theta_0) = 0.000\ 587 + 0.037\ 39 \cos \theta_0 + 0.000\ 063 \cos 2\theta_0$

Recently, a note by Giguère and Srinivasan (14) rejected the structural parameters derived by the Russian authors (3). The note, however, cites the r_e -parameters of Ref. (3) and rejects them because they do not reproduce the B_0 -rotational constants! The r_0 -parameters of Ref. (3) of course reproduce the B_0 -rotational constants quite well—since they were used in the derivation of those parameters.

This work as well as Ref. (7) strongly supports the r_e - and r_0 -parameters from Ref. (3) as the best estimate of the H_2O_2 -structure at present.

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REFERENCES

1. R. L. REDINGTON, W. B. OLSON, AND P. C. CROSS, *J. Chem. Phys.* **36**, 1311–1326 (1962).
2. W. R. BUSING AND H. A. LEVY, *J. Chem. Phys.* **42**, 3054–3059 (1965).
3. G. A. KHACHKURUZOV AND I. N. PRZHEVALSKII, *Opt. Spectrosc.* **36**, 172–174 (1974).
4. E. PRINCE, S. F. TREVINO, C. S. CHOI, AND M. K. FARR, *J. Chem. Phys.* **63**, 2620–2624 (1975).
5. S. W. PETERSON AND H. A. LEVY, *Acta Crystallogr.* **10**, 70–76 (1957).
6. H. KIM, E. F. PEARSON, AND E. H. APPELMAN, *J. Chem. Phys.* **56**, 1–3 (1972).
7. D. CREMER, *J. Chem. Phys.* **69**, 4440–4455 (1978).
8. V. W. LAURIE AND D. R. HERSCHBACH, *J. Chem. Phys.* **37**, 1687–1693 (1962).
9. C. MØLLER AND M. S. PLESSET, *Phys. Rev.* **46**, 618–622 (1934).
10. P. C. HARIHARAN AND J. A. POPLE, *Theoret. Chim. Acta* **28**, 213–222 (1973).
11. (a) R. L. COOK, F. C. DE LUCIA, AND P. HELMINGER, *J. Mol. Spectrosc.* **53**, 62–76 (1974);
(b) A. R. HOY, P. R. BUNKER, *J. Mol. Spectrosc.* **52**, 439–456 (1974).
12. R. H. HUNT, R. A. LEACOCK, C. W. PETERS, AND K. T. HECHT, *J. Chem. Phys.* **42**, 1931–1946 (1965).
13. W. C. OELFKE AND W. GORDY, *J. Chem. Phys.* **51**, 5336–5343 (1969).
14. P. A. GIGUÈRE AND T. K. K. SRINIVASAN, *J. Mol. Spectrosc.* **66**, 168–170 (1977).

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