Short communication

STRUCTURES OF TRIATOMIC RADICALS HCO, HNO AND HOO

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ABSTRACT

New structural parameters have been deduced for the ground electronic states for formyl and hydroperoxyl radicals and nitrosyl hydride, from experimental rotational constants. The values obtained are consistent with known vibrational data and bond dissociation energies.

Four different sets of structural parameters have been proposed for the ground electronic state of the formyl radical HCO. From their own rotational constants B_0 and C_0 for each of HCO and DCO, Herzberg and Ramsay [1] deduced an average CO bond length $R_{CO}^0 = 119.8$ pm and an angle $\alpha^\circ = 119.5^\circ$, assuming $R_{CH}^0 = 108$ pm. These same rotational constants were later used [2] to deduce $R_{CH}^0 = 114.8$, $R_{CD}^0 = 114.5$, $R_{CO}^0 = 117.65$ pm and $\alpha^\circ = 123.3^\circ$. These values were accepted [3] as being correct within the accuracy of the data from optical spectra. The R_{CH} and R_{CD} values reflected the known weakness of the CH (and CD) bond, $D_{H-CO}^0 \leq 0.246$ aJ* [4]; the difference $R_{CH}^0 - R_{CD}^0$ represented a reasonable effect of zero-point energy differences. Shirk and Pimentel [5] used both these rotational constants and vibrational data to produce a structure by minimising error in computed wavenumbers of a group of isotopically substituted molecules in an harmonic approximation. Dixon [6] has shown that the harmonic approximation is poor for this radical; thus the procedure of Shirk and Pimentel is invalid, and the results are meaningless despite their resemblance to the previous set [2].

Recently greatly improved rotational constants of HCO and DCO have become available from microwave spectra [7, 8]. The latter workers reported a structure $R_{CH}^0 = R_{CD}^0 = 111.02 \pm 0.01$ pm, $R_{CO}^0 = 117.115 \pm 0.002$ pm and $\alpha^\circ = 127.426 \pm 0.007^\circ$, but these values combined with the most recent atomic masses [9] and fundamental constants [10] yield rotational constants $B_0 = 44.7758$ and $C_0 = 42.4086$ GHz for HCO and $(B_0 + C_0) =$ 73.6787 GHz for DCO. These rotational constants fail to agree with

^{*}SI metric units are used throughout: $pm = 10^{-12} m$ for internuclear distances, $aJ = 10^{-18} J$ (per molecule) for bond energy, and $mm^{-1} = 10^{-1} cm^{-1}$ for wavenumber units.

the experimental values [7, 8] 44.7774 ± 0.0005 , 41.9410 ± 0.0005 and 73.5339 ± 0.0002 GHz, respectively.

The same procedure as previously [2] has been used to find a correct structure, which reproduces these microwave constants; the results are $R_{CH}^0 = R_{CD}^0 = 114.652 \pm 0.006 \text{ pm}, R_{CO}^0 = 117.825 \pm 0.001 \text{ pm}$ and $\alpha^\circ = 122.724 \pm 0.004^\circ$. This procedure has recently been confirmed in its application to other molecules [11]. If one allows for a difference $R_{CH}^0 - R_{CD}^0 = 0.4 \text{ pm}$, then a better estimate of the true zero-point structure is $R_{CH}^0 - 115.14 \pm 0.03 \text{ pm}, R_{CD}^0 = 114.74 \pm 0.03 \text{ pm}, R_{CO}^0 = 117.708 \pm 0.005 \text{ pm}$ and $\alpha^\circ = 123.01 \pm 0.03^\circ$. These parameters are within experimental error of the previously accepted set [2]. Accordingly this is the structure that ought to be used in theoretical calculations of force constants, etc. [12, 13].

Recently Evenson and co-workers [14] have obtained accurate rotational constants for the hydroperoxyl radical HOO, viz. $A_0 = 2.0358$, $B_0 = 0.11179$ and $C_0 = 0.10566 \text{ mm}^{-1}$. They assumed $R_{OH}^0 = 100.6 \text{ pm}$ and then derived R_{00}^0 132.6 pm and $\alpha^\circ = 108.7^\circ$. Because of the inertial defect effect, it is generally impossible to satisfy all three rotational constants simultaneously within experimental error. The structure just quoted reproduced well A_0 and B_0 but not C_0 . Because A_0 is particularly sensitive to inertial defect corrections, B_0 and C_0 have been used to calculate an alternative set of structural parameters. A better assumed value of R_{OH} is probably 98.2 ± 0.2 pm, because the wavenumbers of the OH stretching vibrations of HOO and s-cisoid HONO are \sim 341.0 mm⁻¹ (in both gas [15] and argon matrix [16] conditions) and 342.5 mm⁻¹ [17], respectively; R_{OH} of HONO has been determined by Cox et al. [18] to be 98.2 pm from microwave spectra, consistent with a good v_{OH} - - R_{OH} correlation. Thus with R_{OH} assumed to be 98.2 pm, the other parameters of HOO are calculated to be $R_{00}^0 = 134.05 \pm$ 0.2 pm and $\alpha^{\circ} = 99.1 \pm 1^{\circ}$. (For the longer $R_{OH}^{0} = 100.6$ pm, the corresponding other parameters are $R_{00}^{\circ} = 133.274 \pm 0.05$ pm and $\alpha^{\circ} = 104.42 \pm 0.4^{\circ}$.)

Accurate microwave rotational constants of nitrosyl hydride HNO have also become available [19]. The exceptional accuracy of these parameters, as well as the inertial defect problem, pose a severe challenge to structure determination. To test a working hypothesis, that a useful estimate of the structure of the zero-point energy state should maintain closely similar magnitudes of R_{NO}^0 and α° of HNO and DNO but permit possibly different R_{NH}^0 and R_{ND}^0 , data for the A ¹A" state of nitrosyl hydride [20] were used; for this state both A_0 , B_0 , C_0 and A_e , B_e and C_e have been derived. With the same computational method as above [2], and requiring $R_{NH}^e = R_{ND}^e$, one obtains $R_{NH}^e = 102.3 \pm 0.4$ pm, $R_{NO}^e = 123.75 \pm 0.01$ pm and $\alpha^e = 115.0 \pm$ 0.6°; these values reproduce B_e and C_e of both HNO and DNO, but not quite A_e , presumably because of the experimental inaccuracy and a residual inertial defect arising from neglect of γ_{rs} (coefficients of $(v_r + \frac{1}{2}) (v_s + \frac{1}{2})$) in determination of A_e , B_e and C_e [21]. Because in this case the experimental error in A_e is both absolutely and relatively (as a fraction of A_e) much larger than that in B_e or C_e , the latter seem more useful for structural determination. If one applies an analogous treatment to the zero-point rotational constants, i.e., requiring the same R_{NO}^0 and α° but permitting $R_{NH} \neq R_{ND}$ to fit the B_0 and C_0 values, one obtains $R_{NH}^0 = 107.0 \pm 0.5$ pm, $R_{NO}^0 = 123.84 \pm 0.08$ pm, $\alpha = 114.25^\circ \pm 0.25^\circ$ and $R_{ND}^0 = 106.4 \pm 0.5$ pm. Comparing these R^e and R^0 parameters, we find R_{NO}^0 slightly exceeds R_{NO}^e , by ~0.1 pm, α^e exceeds α° , by ~0.75°, but R_{NH}^0 and R_{ND}^0 are considerably larger than R_{NH}^e . The bond length increases are expected because of the usual asymmetry of the potential surface cross-section; the angle decrease, to the extent that it is significant, is consistent with a Bastiansen-Morino shrinkage effect [22]. The newly proposed value of $R_{NH}^0 = 107$ pm is better consistent with the wavenumber of the NH stretching mode, 285.417 mm⁻¹ [20], according to extrapolation of Bernstein's [23] correlation plot.

Thus for the ground state zero-point structure of nitrosyl hydride, we can apply the same criteria which seemed to be successful for the excited state, i.e., R_{NO}^0 and α° constant for HNO and DNO and reproducing B_0 and C_0 for both molecules. The results are $R_{NH}^0 = 109.026 \pm 0.05$ pm, $R_{NO}^0 = 120.90 \pm$ 0.01 pm, $\alpha^\circ = 108.047 \pm 0.01^\circ$ and $R_{ND}^0 = 107.951 \pm 0.05$ pm. The unusually large difference $R_{NH}^0 - R_{ND}^0 \sim 1.1$ pm probably indicates the partial failure of the first criterion above, but is also consistent with the small NH dissociation energy, $D_{H-NO}^0 \leq 0.338$ aJ. Furthermore this long bond is appropriate to the small wavenumber of the pertinent stretching vibration, 268.47 mm⁻¹ in the gas phase [24] and 271.1 mm⁻¹ in an Ar matrix [16], again with reference to Bernstein's [23] correlation.

Structural parameters of these three radicals are collected in Table 1. Because these data are all derived essentially from B_0 and C_0 rotational constants, they should be directly comparable.

	R°_{HX} (pm)	$R^{\circ}_{\mathbf{DX}}$ (pm)	$R^{\circ}_{\rm XO}$ (pm)	α° (degrees)
HCO, X ² A'	115.14	114.74	117.708	123.01
HNO, X 'A'	109.026	107.95	120,90	108.047
HNO, A'A"	107.0	106.4	123.84	114.25
HOO, X ² A"	98.2 ^a		134.05	99.1
	(100.6 ^a		133,274	104.42)
HNO, A 'A''	R ^e _{HX} (pm) 102.3	R ^e _{DX} (pm) 102.	R ^e _{XO} (pm) 123.75	α ^e (degrees) 115.0

TABLE 1

Structural parameters of	triatomic radicals HXO
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^aAssumed values,

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