COMMENTS

Comment on "*Ab Initio* Characterization of $HOClO_3$ and HO_4Cl: Implications for Atmospheric Chemistry"

A. I. Karelin

Institute for New Chemical Problems, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russia

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This comment concerns a recent paper in this journal by J. S. Francisco.[1] Using an *ab initio* method, the author determined the harmonic vibrational frequencies and infrared intensities for the $HClO_4$ molecule. He believes that, calculated at the MP2/6-31G (2d, 2p) level of theory, the frequencies are in fair agreement with the spectroscopic data. The comparison is made with the infrared spectra reported by Giguere and Savoie.[2] However, it was shown later[3] that these data were erroneous in that some Cl_2O_7 impurity frequencies were attributed to $HClO_4$. Moreover, the resonance splitting of the $\nu_{as}(ClO_3)$ a′a″band by the δ(OH) a′ mode was not found either.

To eliminate the Cl_2O_7 impurity from $HClO_4$, a special procedure was developed.[4] It was also shown that the resonance splitting results in the three band appearance at 1201 (a′ type), 1265 (a″ type), and 1326 cm^{-1} (a′ type). This splitting disappears upon deuteration, and a single infrared band $\nu_{as}(ClO_3)$ a′a″ is observed at 1282 cm^{-1}.[3]

To establish the true degree of confidence of the *ab initio* spectrum determination, we present, for comparison, the refined experimental frequencies as well as infrared relative intensities taken ref 3 in Table 1. The comparison shows that the agreement between the *ab initio* and experimental frequencies is rather poor for ν_2, ν_9, and ν_{11} modes. The indicated *ab initio* ν_2, ν_9, and ν_{11} frequencies agree well only with the data recorded in ref 2. A considerable discrepancy is observed between the calculated and experimental infrared intensities for ν_2, ν_3, and ν_9 and especially for ν_{11} modes. This leads one to the conclusion that a satisfactory reproduction of the $HClO_4$ vibrational spectra at the present level of *ab initio* methods is still a hard task.

TABLE 1: Calculated *ab Initio* Vibrational Parameters and Experimental Infrared Data for $HClO_4$

		frequencies (cm^{-1})		relative intensities	
	mode no.	calc [1]	expt [3]	calc [1]	expt [3]
a′	1	3554	3553	0.4	0.4
	2	1225	1326	1.0	0.6
	3	1215	1201	0.6	0.4
	4	1016	1048	0.3	0.5
	5	690	726	0.7	1.0
	6	551	582	0.1	*a*
	7	526	555	0.007	
	8	395	421	0.01	*b*
a″	9	1333	1265	0.6	0.9
	10	552	582	0.07	*a*
	11	500	421	0.3	*b*
	12	357		0.03	

[a] $(D\nu_6 + D\nu_{10})/D\nu_5 = 0.2$ (calculated value is 0.2). [b] $(D\nu_8 + D\nu_{11})/D\nu_5 = 0.02$ (calculated value is 0.4).

Of greater interest are the calculations on the equilibrium structure of $HClO_4$ performed at various levels of *ab initio* theory both by Francisco[1] and by Casper et al.[5] Surprisingly, Francisco does not even make reference to the data in ref 5, which were also published in this journal. The minimum-energy structure calculation performed by both groups of authors at all levels revealed that the hydrogen atom on $HClO_4$ prefers to orient in the staggered position and also indicated a small ClO_3 group distortion. These data are consistent with the known peculiarities of the $HClO_4$ gas infrared spectrum.[3] Indeed, the resonance splitting of the $\nu_{as}(ClO_3)$ a′a″ band is a consequence of the OH group preferential orientation. The accidental degeneracy of ν_6 and ν_{10} modes as well as ν_8 and ν_{11} modes indicates the ClO_3 group symmetry is very close to C_{3v}. On the other hand, the $\nu_{as}(ClO_3)$ a′a″ band of $DClO_4$ (C_s) is broader than the corresponding $\nu_{as}(ClO_3)$ e band of $FClO_3$ (C_{3v}), which suggests some small distortion of ClO_3 group. The half-width of those bands is 50 and 34 cm^{-1} for $DClO_4$ and $FClO_3$, respectively. The $\nu_{as}(ClO_3)$ a′a″ band splitting apparently does not exceed 15 cm^{-1} for $DClO_4$.

In contradiction with the infrared data, Francisco[1] concludes that the hydrogen atom rotates freely about the $OClO_3$ group at room temperature. His conclusion is based upon the estimation of the 3-fold potential barrier, which is 0.59 kcal mol^{-1} at the MP-2/6-31G (2d, 2p) level. As he states, since there is free rotation, this suggests that ClO bonds measured by the electron diffraction studies may represent a group average. Akishin et al.[6] and Clark et al.[7] did not reveal (or did not try to find) any distortion of the ClO_3 group in actuality, performing the appropriate gas $HClO_4$ experiments. However, carrying out a joint gas $HClO_4$ electron diffraction and microwave spectroscopic study, Casper et al.[5] found that it was not possible to fit the diffraction intensities and rotational constants simultaneously, assuming C_{3v} symmetry for the ClO_3 group.

It is interesting to note that no ClO_3 group distortion was found for parent $FOClO_3$, $ClOClO_3$, and Cl_2O_7 molecules by the gas electron studies and *ab initio* calculations.[5,8]

References and Notes

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