FORMALDEHYDE AND ACETALDEHYDE PHOTODISSOCIATION IN THE EXCITED STATE S_2

V.Ya. Artyukhov, N.A. Zvereva, I.I. Ippolitov, and A.F. Terpugova

V.D. Kuznetsov Siberian Physicotechnical Institute
at the State University, Tomsk

Received April 1, 1994

The subject of this theoretical study was the low excited singlet state S_1 of formaldehyde and acetaldehyde and their radical dissociation. Investigation into the dissociation from the S_1 state was carried out using ab initio method. The activation barriers were determined for formaldehyde and acetaldehyde with correction made for energy of zeroth vibrations to be 66.9 *and* 56.5 kcal/mole*, respectively. The analysis of mechnisms of dissociation from S_1 and S_2 excited singlet states was done based on calculated constans of photodissociation and intercombination conversion rates as well as the pecular features of the potential surfaces of these aldehydes. A possibility of using the spectroscopy of photofragments for identification of the aldehydes in their mixtures was studied. Based on calculated constants of the dissociation rate K_d and Frank–Condon factors the signal of fluorescence* $CHO(^2\Pi) \rightarrow CHO(^2A') + h\nu$ *was estimated as a function of the photolytic wavelength.*

INTRODUCTION

Aldehydes play an important role in photochemistry of atmospheric pollution. On the one hand, they are present in anthropogenic discharges into the atmosphere, on the other hand, they are products of a number of phototechnical reactions. The aldehyde photodissociation processes are the substantial source of radical and molecular products of disintegration. Formaldehyde H_2CO and acetaldehyde CH_3CHO being the simplest aldehydes occupy, from this viewpoint, the great attention of scientists.[1–3,16–17]

Authors of Ref. 1 have theoretically analyzed the process of formaldehyde dissociation on the potential surface S_0 in details. According to Ref. 1 the formaldehyde dissociation into molecular products follows the scheme

$$H_2CO\,(S_0) + h\nu \rightarrow H_2CO\,(S_1) \rightarrow H_2CO^*\,(S_0) \rightarrow H_2 + CO\ . \quad (1)$$

The process (1) proceeds through energy barrier on S_0 surface with the height founded to be $\Delta S_0^{\neq} = 87$ kcal/mole (3.79 eV, 30 537 cm^{-1}). The energy of zeroth vibrations is included into presented value.

The experimental value of activation barrier $\Delta S_0^{\neq} = (78 - 81)$ kcal/mole together with that calculated with allowance for zeroth vibrational energy $\Delta S_0^{\neq} = 81.4$ kcal/mole, which are in good agreement with each other, are presented in Ref. 16.

The process of disintegration into radical products follows the scheme:

$$H_2CO\,(S_0) + h\nu \rightarrow H_2CO\,(S_1) \rightarrow H_2CO^*(T_1) \rightarrow H + HCO\,(^2A_1) \quad (2)$$

The height of barrier $\Delta T_1^{\neq} = 96.7$ kcal/mole (4.21 eV, 33 942 cm^{-1}) for this reaction is presented in Ref. 1, where the possibility of radical dissociation from S_0 state without transient states formation (87.5 kcal/mole, 3.79 eV, 30 600 cm^{-1}) and intramolecular reconstruction into hydroxycarbene (89 kcal/mole, 3.85 eV, 31 000 cm^{-1}) is noted.

Reference 17 gives the experimental value of activation barrier $\Delta T_1^{\neq} = (90 - 93)$ kcal/mole. The dissociative mechanism of formaldehyde triplet is considered in this paper. The rate of intercombination conversion was previously considered to be small in comparison with $S_1 \rightarrow S_0$ relaxation (or radical course of reaction on S_0 surface) and, consequently, the T_1 mechanism was out of importance. The study[17] demonsrated that barrier for T_1 was the result of superposition of three electronic states, namely, $(n \rightarrow \pi^*)$, $(\pi \rightarrow \pi^*)$, and $[n(\sigma) \rightarrow \sigma^*]$. This superposition was described in terms of two- and three-dimentional triplet states. Changing molecular geometry leads to reduction of symmetry, causes interaction of three states, and gives rise to new superpositions of low triplet states.

The similar calculations for acetaldehyde CH_3CHO were performed in Ref. 2. The values were found $\Delta S_0^{\neq} = 84.4$ kcal/mole (3.67 eV, 29 624 cm^{-1}) for the barrier of molecular dissociation into CH_4 and CO and $\Delta T_1^{\neq} = 89.1$ kcal/mole (3.88 eV, 31 274 cm^{-1}) for that of radical dissociation into CH_3 and HCO ($^2A_1$).

1. ALDEHYDE PHOTODISSOCIATION AT EXCITED S_1 STATE

The estimations presented above allow the processes of disintegration of H_2CO and CH_3CHO at excited S_1 state to be forecasted. It should be noted that when zeroth vibrational state of S_1 (80.6 kcal/mole, 3.51 eV, 28 290 cm^{-1} for formaldehyde and 82.5 kcal/mole, 3.59 eV, 28 597 cm^{-1} for acetaldehyde) being excited, the disintegration is unlikely because for acetaldehyde the barrier for any one of the reaction schemes exceeds the value given above, and for formaldehyde $\Delta S_0^{\neq} = (78 - 81)$ kcal/mole, $\Delta S_1 = 80.6$ kcal/mole, and $\Delta T_1^{\neq}$ is greater than ΔS_1.

0235-6880/94/09 658-05 $02.00

As upper vibrational levels are excited, the following processes are bound to start subsequently: disintegration into radicals from S_0 state, intramolecular reconstruction, and disintegration into radicals from T_1 state.

The existing experimental data[4–8] confirm this sequence as a whole. However, there is unambiguous evidence that the dissociation process can proceed rather effectively from the states with energies less than the barrier, i.e., due to tunneling.[4,6]

The processes discussed above proceed after original act, the optical excitation of one rovibronic level of S_1 state, and subsequent radiationless transfer of excitation energy into S_0 and T_1 states via the mechanisms of internal and intercombination conversion.

We attempted to evaluate the possibility of radiationless energy transfer for S_1 and T_1 electronic states using INDO/CL semiempirical theory.[14] The obtained values of intercombination conversion constants in molecular geometry changing at $S_0 \rightarrow T_1$ and $S_0 \rightarrow S_1$ transitions are as follows:

formaldehyde $K_{S_1T_1} = 2.2\cdot10^6$, $K_{S_1T_1^{\neq}} = 6.5\cdot10^6$,
acetaldehyde $K_{S_1T_1} = 2.7\cdot10^8$, $K_{S_1T_1^{\neq}} = 6.1\cdot10^8$.

These constants equal zero at equilibrium geometry S_0.

Because semiempirical approach is the base for these results, they cannot be considered as accurate enough. But they give the qualitative pattern of geometry effect on the spin-orbital interaction. It is clear that the geometry change, or molecular symmetry reduction, leads to intercombination conversion constant increasing several orders of magnitude. Consequently, when exciting S_1 state, the dissociative mechanism on T_1 surface play an important part.

The reaction of radical disintegration seems to be preferential from the viewpoint of optical methods development for diagnostics of particular aldehydes in their mixture, because the formyl radical HCO ($^2A_1$) can be succesfully detected using method of laser–induced fluorescence.[8]

2. ALDEHYDE PHOTODISSOCIATION AT EXCITED S_2 STATE

The formyl radical formation in the first excited state of HCO ($^2\Pi$) allows the passive detection of fluorescence followed by radiative disintegration of this state. According to Refs. 1 and 2 the energy of products of radical disintegration $\mathrm{H}(^2S) + \mathrm{HCO}(^2\Pi)$ is 113.5 kcal/mole (4.93 eV, 39 838 cm^{-1}) for formaldehyde and 102 kcal/mole (4.43 eV, 35 801 cm^{-1}) for acetaldehyde $\mathrm{CH_3}(^2A_2'') + \mathrm{HCO}(^2\Pi)$.

Using these values as the base, the barriers for the reactions with HCO($^2\Pi$) should be searched for on the S_1 surfaces. We calculated the sections of potential surfaces $\mathrm{H_2CO}(S_1)$ and $\mathrm{CH_3CHO}(S_1)$ along the reaction coordinate, the bond lengths $R_{\mathrm{C-H}}$ for formaldehyde and $R_{\mathrm{C-C}}$ for acetaldehyde were chosen as those. The calculations were carried out using MONSTERGAUSS program with 6–31G^* basis, which describes the peculiarities of potential surfaces adequately. Fragment optimization was not carried out when $R_{\mathrm{C-H}}$ and $R_{\mathrm{C-C}}$ varying. Figures 1 and 2 show the curves obtained in such a way for $\mathrm{H_2CO}$ and $\mathrm{CH_3CHO}$, respectively. As seen from these figures there exist transient states at $R_{\mathrm{C-H}}$ = 1.8Å for formaldehyde and $R_{\mathrm{C-C}}$ = 2.2Å for acetaldehyde. The height of activation barrier $\Delta S_1^{\neq}$ for $\mathrm{H_2CO}$ is 71 kcal/mole without regard for zeroth vibrations and 66.9 kcal/mole with regard to zeroth vibrations. For $\mathrm{CH_3CHO}$ these values are 65.5 kcal/mole and 56.5 kcal/mole, respectively. The numerical results given above are presented in Figs. 3 ($\mathrm{H_2CO}$) and 4($\mathrm{CH_3CHO}$) in diagram form. As seen from diagrams, at excitation of S_1 state and subsequent $S_2 \rightarrow S_1$ conversion, the disintegration channel with formation of CHO($^2\Pi$) and subsequent reaction of radiative disintegration is energetically allowed

$$\mathrm{CHO}\,(^2\Pi) \rightarrow \mathrm{CHO}\,(^2A') + h\nu'. \qquad (3)$$

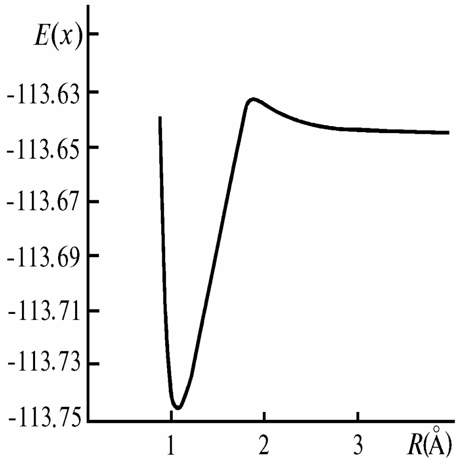

FIG. 1. Formaldehyde potential function in S_1 electronic state when stretching the C–H bond

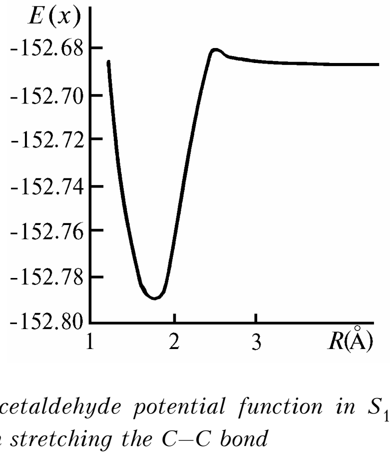

FIG. 2. Acetaldehyde potential function in S_1 electronic state when stretching the C–C bond

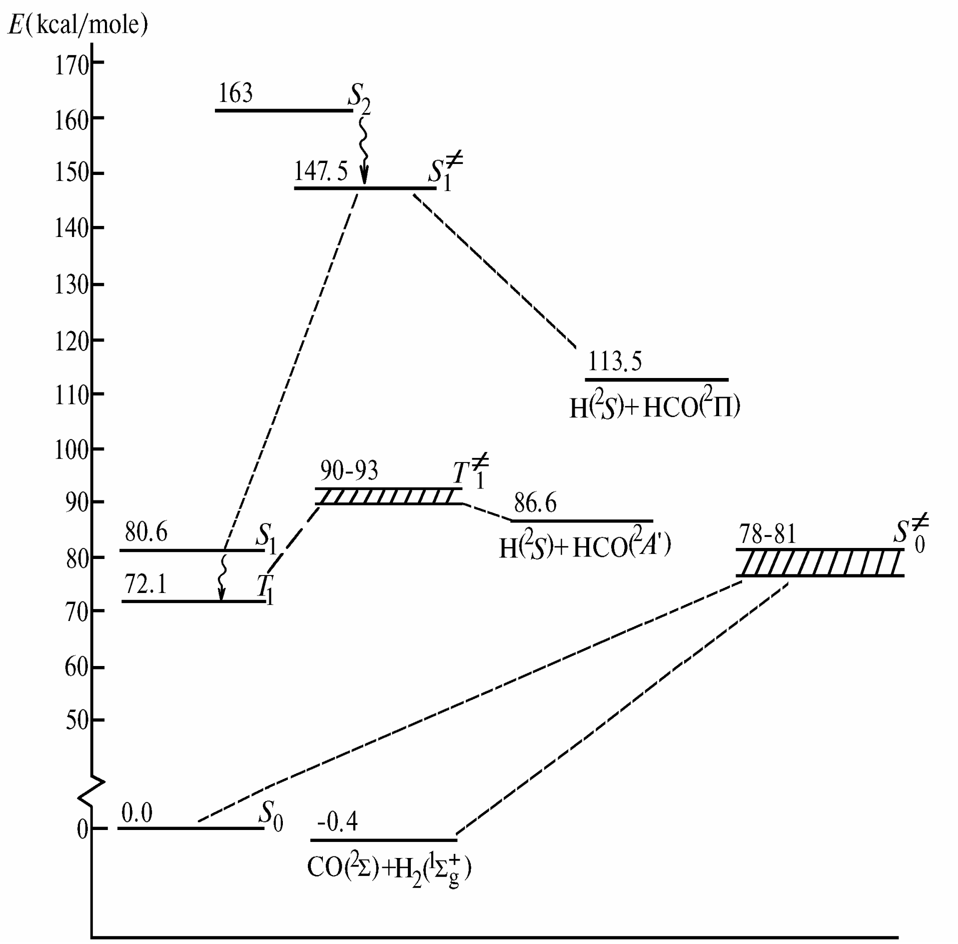

FIG. 3. Diagram of formaldehyde energy levels and dissociation barriers

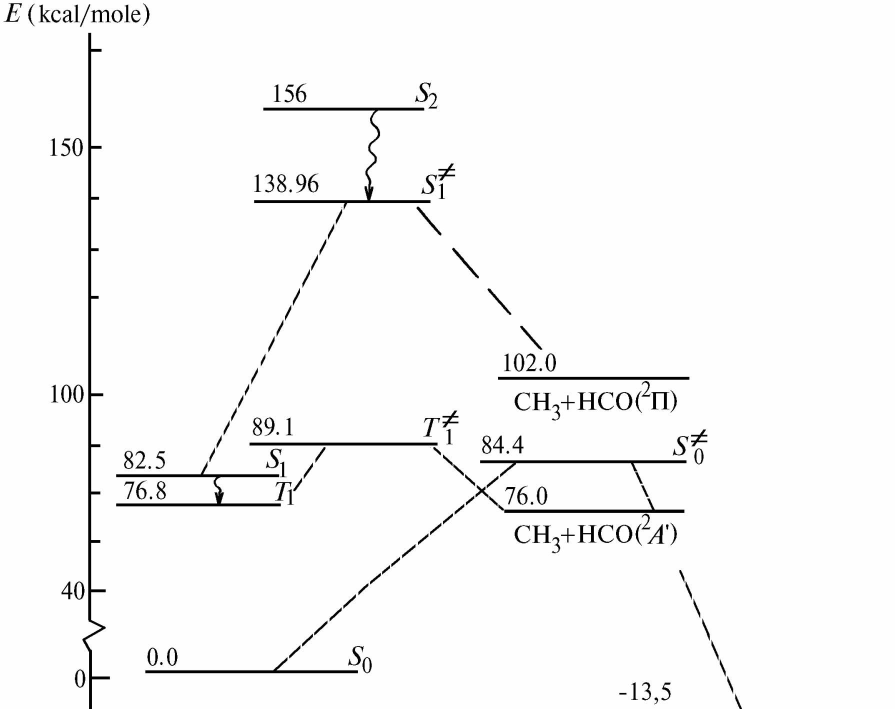

FIG. 4. Diagram of acetaldehyde energy levels and dissociation barriers

Let us consider now the situation, when the admixtures of formaldehyde and acetaldehyde to be detected are in analyzed gaseous mixture. Let us take into account the circuimstance: the S_2 state of formaldehyde lies somewhat above S_2 state of acetaldehyde (163 kcal/mole and 156 kcal/mole, see Ref. 9). Then the excitation of zeroth vibrational level of acetaldehyde ($\lambda \simeq 182$ nm) and subsequent internal conversion $S_2 \to S_1$ can lead to formation of overexcited with respect to barrier $\Delta S_1^{\neq}$ molecules and their subsequent dissociation via the channel with radicals HCO($^2\Pi$) formation. The latter can undergo the radiative disintegration following the reaction (3), and the fluorescence signal can be detected on frequency ν'. In this case the formaldehyde molecules will be excited due to transitions into upper vibrational levels of S_1 state. However, the probability of such transitions is small in accordance with Frank–Condon principle. If the photolytic wavelength decreases to $\lambda \cong 175$ nm, then the new process starts, the excitation of S_2 state of formaldehyde. In doing so the detected signal at frequency ν' should abruptly increase. The degree of this increase can be evaluated by calculation of dissociation rate for H_2CO and CH_3CHO in the frame of semiclassical approximation of RRKM theory[10]

$$K(E) = c\,\mathrm{L}\left(\prod_{i=1}^{s} \nu_i\right) \Big/ \left(\prod_{i=1}^{s} \nu'_i\right)\left(\frac{E - \Delta S_1^{\neq}}{E}\right)^{s-1}, \quad (4)$$

where ν_i and ν'_i are the vibrational frequencies of a molecule and activated complex in the S_1 state; E is the excitation energy counted off from zeroth vibrational level of S_1 state; s is the number of vibrational degrees of freedom; and, c is the speed of light. The data on vibrational frequencies were borrowed from Ref. 1 for H_2CO and from Ref. 11 for CH_3CHO when calculating. The obtained results for $K(E)$ are presented in Fig. 5. Let us denote the rates of radiative excitation of S_2 state as W^{f} and W^{a} for formaldehyde and acetaldehyde, respectively, and the rates of disintegration of S_2 state with formation of CHO ($^2\Pi$) as K^{f} and K^{a}. Now the degree of change of fluorescent signal at frequency ν' is proportional to the ratio

$$\frac{W^{\mathrm{a}}(175)\,K^{\mathrm{a}}(175) + W^{\mathrm{f}}(175)\,K^{\mathrm{f}}(175)}{W^{\mathrm{a}}(182)\,K^{\mathrm{a}}(182) + W^{\mathrm{f}}(182)\,K^{\mathrm{f}}(182)}. \quad (5)$$

Then, as follows from Figs. 3, 4, and 5

$K^{\mathrm{a}}(175) \sim 5{\cdot}10^7\ \mathrm{s}^{-1}$, $K^{\mathrm{f}}(175) \sim 5{\cdot}10^{10}\ \mathrm{s}^{-1}$,
$K^{\mathrm{a}}(182) \sim 10^6\ \mathrm{s}^{-1}$, $K^{\mathrm{f}}(182) \sim 10^9\ \mathrm{s}^{-1}$.

The rate of radiative transition between two rovibronic states is known to be proportional to Frank–Condon factor F. To evaluate the latter one, we use the approximate equation:[12]

$$F_{0\to n} = |\langle 0 \mid n \rangle|^2 = y^n (n\,!)^{-1} \exp(-y), \quad (6)$$

where n is the number of vibrational levels at upper electronic state; $y = \mu\omega\Delta^2/2\hbar$; ω is vibrational frequency of oscillator; μ is reduced mass; and, $\Delta = R_0 - R'_0$ is the change of equilibrium position 0–0 of transition between S_0 and S_2 states of acetaldehyde ($\lambda = 182$ nm). The value of Δ (change of length of C–C bond at transition) is only 0.024 a.u. (see Ref. 13), consequently $F^{\mathrm{a}}_{0\to 0}(182) \simeq 1$.

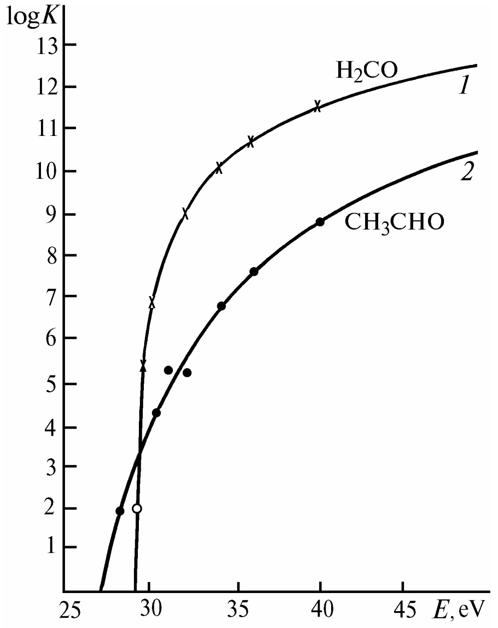

FIG. 5. Constant of photodissociation RCOH + hν → R + COH rate vs. excitation energy for formaldehyde (1) and acetaldehyde (2)

For formaldehyde this wavelength falls into region of excited vibrational levels of S_1 state. For antisymmetric vibrations of C–H bonds the frequency changes from 2843.4 cm^{-1} in S_0 state to 2968 cm^{-1} in S_1 state. Consequently, the radiation 182 nm in wavelength will excite the vibration with quantum number $n \simeq 9$ in formaldehyde. If one takes into account that C–H bond lengths at $S_0 \to S_1$ transition change by $\Delta \simeq 0.01$ a.u., then it follows from Eq. 6 that $F^{\mathrm{f}}_{0\to 9}(182) \simeq 0$. If now the 0→0 transition between S_0 and S_2 states of formaldehyde ($\lambda = 175$ nm) is excited, then $F^{\mathrm{f}}_{0\to 0}$ (182) $\simeq 1$. In acetaldehyde this wavelength excites the C–C bond vibration with 1055 cm^{-1} frequency[13] and vibrational quantum number $n \simeq 2$. For this transition $F^{\mathrm{a}}_{0\to 2}$ (175) $\simeq 2.25{\cdot}10^{-6} \sim 0$. Then Eq. (5) takes the form

$$\frac{f^{\mathrm{f}}}{f^{\mathrm{a}}}\frac{K^{\mathrm{f}}(175)}{K^{\mathrm{a}}(182)} \simeq 5\cdot 10^4 f^{\mathrm{f}}/f^{\mathrm{a}} = 5{\cdot}10^4\cdot 0.889/0.427 = 1.145{\cdot}5{\cdot}10^4,$$

where f^{f} and f^{a} are the oscillator strengths of electronic transitions $S_0 \to S_2$ for formaldehyde and acetaldehyde. The marked difference in fluorescence signals for two discussed values of photolytic wavelength allows the concentration of each aldehyde to be determined using the expressions, which relate the fluorescence signal power with the concentration of the molecules in S_0 state[15].

ACKNOWLEDGEMENT

This work was partially supported by personal Grant of Special Foundation for Financian Support of Young Gifted Scientist, Russia.

REFERERENCES

1. J.D. Goddard and H.F. Schaefer, J. Chem. Phys. **70**, No. 11, 5117–5134 (1979).

2. J.S. Yadav and J.D. Goddard, J. Chem. Phys. **84**, No. 5, 2682–2690 (1986).

3. N.A. Zvereva, I.I. Ippolitov, and A.F. Terpugova, Izv. Vyssh. Uchebn. Zaved., Ser. Fizika, No. 3, 121–122 (1993).

4. H.L. Dai, R.W. Field, and J.L. Kinsey, J. Chem. Phys. **82**, No. 3, 1606–1607 (1985).

5. C. Cheng, P. Ho, C.B. Moore, and M.B. Zughul, J. Phys. Chem. **88**, No. 2, 296–300 (1984).

6. A. Horowitz and J.G. Calvert, Int. J. Chem. Kinet., No. 10, 713–720 (1978).

7. F. Stoeckel, M. Schuh, N. Goldstein, and G.N. Atkinson, Chem. Phys. **95**, No. 1, 135–144 (1985).

8. B.M. Stone, M. Noble, and F. Lee, Chem. Phys. Lett. **118**, No. 1, 83–87 (1985).

9. O.V. Sverdlova, *Electronic Spectra in Physical Chemistry* (Khimiya, Leningrad, 1973), 248 pp.

10. P.I. Robinson and K.A. Holbrook, *Unimolecular Reactions* (Wiley, New York, 1972).

11. N.A. Zvereva, I.I. Ippolitov, and A.F. Terpugova, Atm. Opt. **4**, No. 1, 55–59 (1991).

12. G.V. Mayer and V.I. Danilova, *Quantum Chemistry, Molecular Structure and Photonics* (State University, Tomsk, 1984), 218 pp.

13. J.S. Crighton and S. Bell, J. Mol. Spectrosc. **112**, No. 2, 285–303 (1985).

14. V.Ya. Artyukhov and A.I. Galeeva, Izv. Vyssh. Uchebn. Zaved., Ser. Fizika, No. 11, 96–100 (1986).

15. N.A. Zvereva, I.I. Ippolitov, and A.F. Terpugova, Izv. Vyssh. Uchebn. Zaved., Ser. Fizika, No. 9, 86–87 (1992).

16. G.E. Scuseria and H.F. Schaefer III, J. Chem. Phys. **90**, No. 7, 3629–3636 (1989).

17. B.F. Yates, Y. Yamaguchi, and H.F. Shaefer III, J. Chem. Phys. **93**, No. 12, 8798–8807 (1990).