# $S_1 \leftarrow S_0$ Vibronic spectra and the structure of acetyl fluoride-$h_3$ and acetyl fluoride-$d_3$ molecules

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UV absorption spectra of acetyl fluoride-$h_3$ and -$d_3$ ($CH_3COF$ and $CD_3COF$) molecules in the region of $S_1 \leftarrow S_0$ electronic transitions are investigated. The origins ($0^0{}_0$ or $14^{0\pm}{}_0$) of these transitions are observed at 39912 and 39904 $cm^{-1}$, respectively, and some of the fundamental frequencies of these molecules in the $S_0$ and $S_1$ states are determined. In particular, the systems of torsion and inversion (out-of-plane C=O vibrations) energy levels are studied. The geometric parameters of an acetyl fluoride-$h_3$ molecule in the $S_1$ state are estimated by the theoretical simulation of the rotational contours of the $0^0{}_0$ ($14^{0\pm}{}_0$) band. These data are used to evaluate the potential barriers to internal rotation in the $S_0$ and $S_1$ states, which were found to be 360 and 560 $cm^{-1}$ for acetyl fluoride-$h_3$ and 380 and 770 $cm^{-1}$ for acetyl fluoride-$d_3$, respectively, as well as the potential barriers to inversion in the $S_1$ states, which were found to be 2090 and 2370 $cm^{-1}$ for acetyl fluoride-$h_3$ and acetyl fluoride-$d_3$, respectively.

**Key words:** vibronic spectra, structure, acetyl fluoride, potential barrier, internal rotation, inversion.

Vibronic spectra, structure, and conformations of the molecules of carbonyl compounds have been studied in this laboratory for several years.[1] In particular, previously we reported[2,3] the results for acetaldehyde-$h_4$ and -$d_4$, as well as for acetone-$h_6$ and -$d_6$. Recently, studies have been done on acetyl halide molecules with the general formula $R_1COR_2$, where $R_1$ = $CH_3$ and $CD_3$, $R_2$ = F, Cl, and Br. The present paper concerns the vibrational analysis of the $S_1 \leftarrow S_0$ electronic transition ($S_1$ and $S_0$ are the ground and first excited singlet electronic states, respectively) in the acetyl fluoride-$h_3$ and -$d_3$ ($CH_3COF$ and $CD_3COF$) molecules, which henceforth will be designated as AF-$h_3$ and AF-$d_3$. The results for acetyl chloride and acetyl bromide molecules have been published elsewhere.[4,5]

An earlier analysis of the microwave spectra for eight isotopic modifications of AF molecule established the geometric parameters of this molecule in the $S_0$ state.[6] Furthermore, the height of the potential barrier to inversion was evaluated as $V_3$ = 364 $cm^{-1}$ from the torsion splitting of the ground vibrational level of AF-$h_3$ molecule.[6] In this analysis the potential function of internal rotation was presented as the series

$$V(\varphi) = \frac{1}{2} \sum_n V_n (1 - \cos n\varphi) \qquad (1)$$

where $\varphi$ is the angle of internal rotation, and only one harmonic with $n$ = 3 was included.

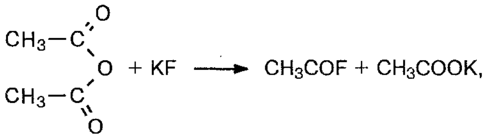
Vibrational spectra of AF-$h_3$ and AF-$d_3$ were also investigated and all fundamental frequencies except the torsion ones were determined.[7—9]

Studies on the vibronic spectra of the related formaldehyde,[10,11] formyl fluoride,[12,13] formyl chloride,[14] acetaldehyde,[15,16] and acetone[3,16,17] revealed that carbonyl fragments of these molecules are nonplanar in the $S_1$ state (in contrast to the $S_0$ state, in which the carbonyl fragments are planar). Moreover, for the two latter molecules the orientations of the methyl tops are significantly distinct in the $S_0$ and $S_1$ states (for each molecule the potential minima in the $S_1$ state are markedly shifted from those in the $S_0$ state along the internal rotational coordinate). Therefore, the question of whether or not such differences are pertinent to the structures of AF molecules in the $S_0$ and $S_1$ states appears to be of interest.

## Experimental

The investigations of the spectra were carried out for two samples synthesized by two methods

$$2\,CH_3COCl + ZnF_2 \longrightarrow 2\,CH_3COF + ZnCl_2, \qquad (2)$$



$$(CH_3CO)_2O + KF \longrightarrow CH_3COF + CH_3COOK, \qquad (3)$$

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The use of two synthetic pathways (2)[18] and (3)[19] were used for the following reason. Since AF is a very reactive compound, it is difficult to analyze the purity of the sample by chromatography, whereas the vibrational spectroscopy and proton magnetic resonance methods, which may be used for purity control, can be less sensitive than UV spectroscopy. On the other hand, the possible impurities should be different in different syntheses, so they can be detected by comparing vibrational, NMR, or UV spectra of two samples.

We found, however, that IR spectra of both samples are identical and that they coincide with that given in the literature.[9] In addition, no impurities could be observed in $^1$H NMR spectra. Gas-phase vibronic (UV) spectra for the two AF samples were also virtually identical, although very weak vibronic bands of acetyl chloride were detected for the sample obtained by reaction (2). For these reasons, the AF-$d_3$ molecule was synthesized by reaction (3) and all future investigations of the AF-$h_3$ molecule were performed with a sample obtained in the same way.

First, the low-resolution gas-phase UV spectrum of AF-$h_3$ molecule was recorded using a "Specord-M40" spectrophotometer. A fragment of this spectrum is presented in Fig. 1. Second, for AF-$h_3$ and AF-$d_3$ molecules in gas phase at room temperature, UV spectra of intermediate resolution were obtained near the first (long-wave) absorption band (2350—2630 Å), which corresponds to the $S_1 \leftarrow S_0$ electronic transition. These spectra were recorded using a multipass optical cell with the path length ranging from 5 to 40 m, and the partial pressure of the substance under study ranging from 1 to 100 Torr. To avoid the interaction of the AF molecule with aluminum cover of the glass spherical bases of focusing mirrors in the cell, mirrors protected by a $MgF_2$ layer were used. Nevertheless, the mirrors were replaced several times in the course of experiments due to the deposit formation.

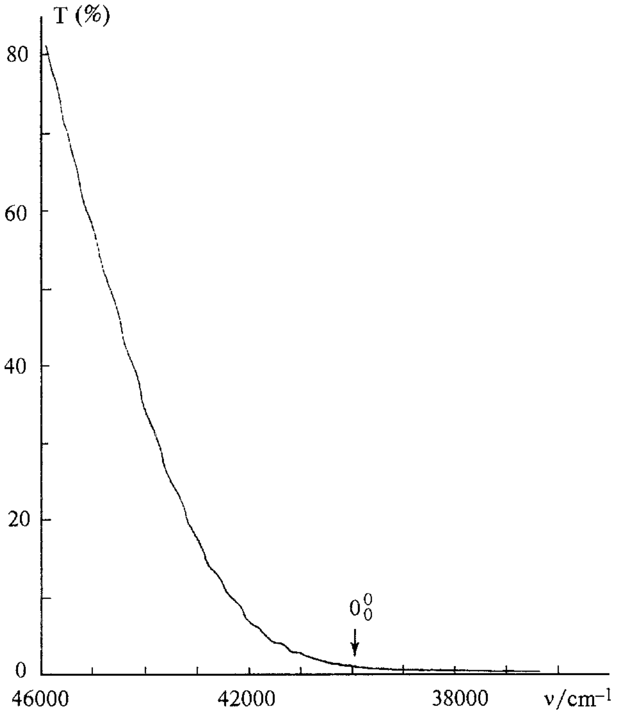

**Fig. 1.** The fragment of low-resolution absorption spectrum of acetyl fluoride-$h_3$ in the gas phase recorded in the 10 cm cell. Arrow indicates the origin of electronic transition ($0^0{}_0$ or $14^{0\pm}{}_0$ transition) determined by the analysis of the vibrational structure in the UV spectrum of intermediate resolution.

The spectra were registered photographically by a DFS-452 spectrograph with the first order of diffraction grating of 2400 lines/mm with theoretical resolution ability of 120000. The spectrum of an Fe—Ne hollow cathode lamp was used as a reference. Then microphotograms of these spectra were obtained (see Fig. 2).

The bands in the intermediate region of AF-$h_3$ and AF-$d_3$ UV spectra are mainly doublets (see Fig. 2) with the distance between peaks 9—11 and 7—9 cm$^{-1}$ for AF-$h_3$ and AF-$d_3$, respectively. They were measured with 0.5—1.0 cm$^{-1}$ accuracy from the low frequency peaks on the photoplates using a comparator. In the high-frequency regions of the spectra the bands spread out and look like broad singlets. They were measured from the maxima with the accuracy of several cm$^{-1}$. The wavenumbers of all observed bands were adjusted to vacuum.

## Results and Discussion

Although the bands in UV spectra of the AF-$h_3$ molecule are more intense and sharp than those of the AF-$d_3$ molecule (see Fig. 2), both spectra are qualitatively similar, exhibiting more than twenty repetitive characteristic groups of the bands. The intervals between bands and intensity distributions in these groups, in turn, are very close to those in characteristic groups in UV absorption spectra of acetaldehyde-$h_4$ and -$d_4$ molecules (for the $T_1 \leftarrow S_0$ transitions), which were assigned to the vibronic transitions between torsion levels of the $S_0$ and $T_1$ electronic states.[2,20] Accepting these analogies as well as the estimations of torsion frequencies (more precisely, the frequencies of the $0E \leftarrow 1E$ torsion transitions) of the AF-$h_3$ and AF-$d_3$ molecules in the $S_0$ state as 121 and 92 cm$^{-1}$, respectively (these values were calculated by numerical solution of one-dimensional Schrödinger equation[21] for the geometry and using the barrier to internal rotation determined from microwave spectra[6]), we assigned to these ($0E \leftarrow 1E$) torsion transitions 115 and 94 cm$^{-1}$ differences between vibronic bands in the characteristic groups of AF-$h_3$ and AF-$d_3$, respectively. From this assignment other bands in the characteristic groups of AF-$h_3$ and AF-$d_3$ molecules can be attributed as shown in Table 1 (for each molecule the most intense group of observed bands is chosen).

As was mentioned above, in the spectra of the AF-$h_3$ and AF-$d_3$ molecules, more then twenty characteristic groups of bands are observed. One of them (for each molecule) can be connected with the origin of the $S_1 \leftarrow S_0$ electronic transition, *i.e.*, with the transition between ground vibrational levels of the $S_1$ and $S_0$ states, whereas others correspond to "pseudoorigins", *i.e.*, the transitions of $M^{v'}{}_{v''} \ldots N^{v'}{}_{v''}$ type, where $M$, $N$ are the numbers of vibrational modes and $v'$, $v''$ denote their vibrational quantum numbers in the $S_0$ and $S_1$ states, respectively. We assume that, as in other molecules of carbonyl compounds, the origins of the $S_1 \leftarrow S_0$ transi-

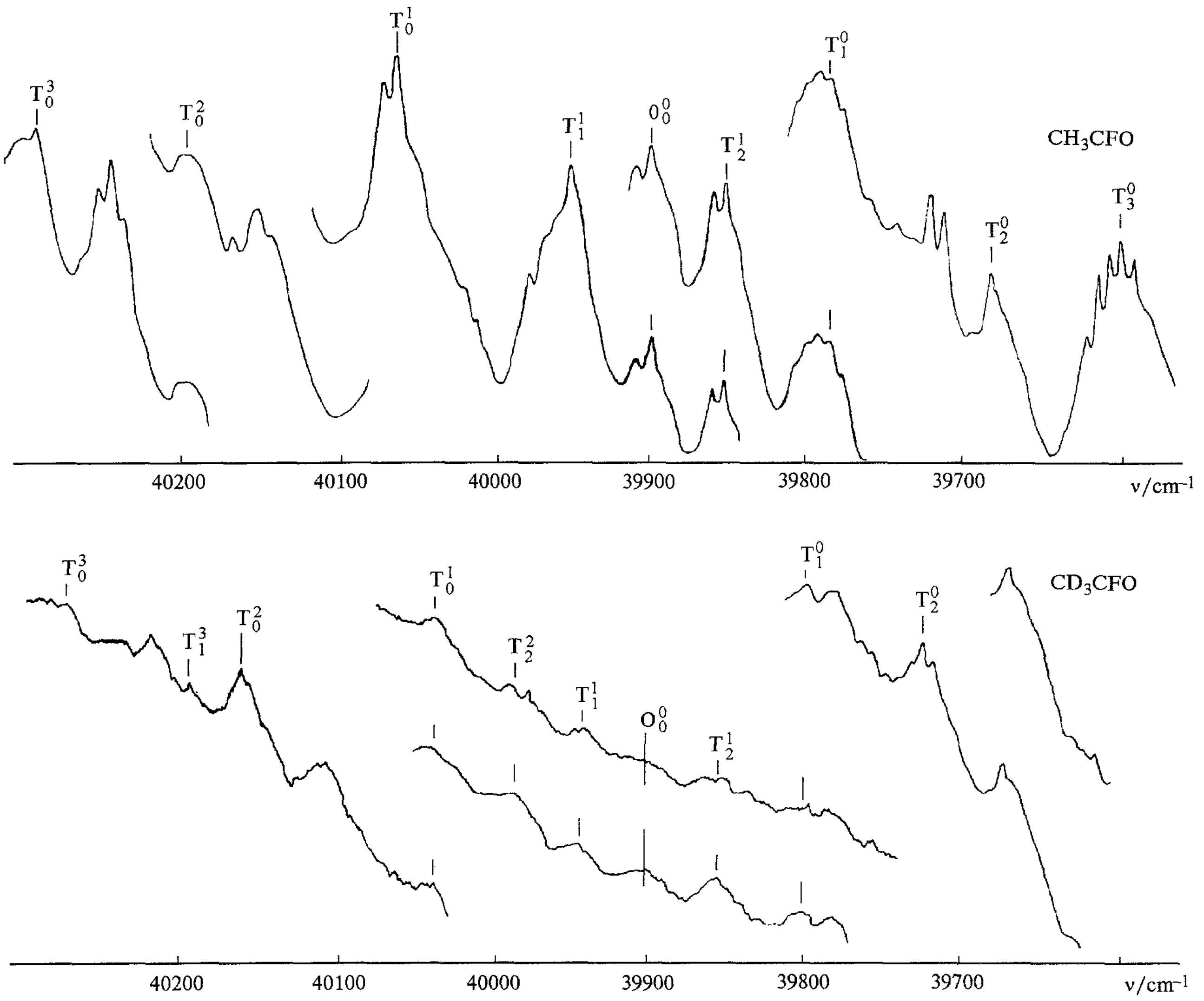

**Fig. 2.** Microphotograms of the fragments of the intremediate-resolution UV spectra of the AF-$h_3$ and AF-$d_3$ vapours in the region of $0^0_0$ ($14^{0\pm}_0$) transitions (the bands corresponding to the transitions between $S_0$ and $S_1$ torsion levels are marked by letter "T").

**Table 1.** Assignment of the bands constituing the characteristic groups in the UV spectra of AF-$h_3$ and AF-$d_3$ molecules (cm$^{-1}$)

| $\nu_i$ | $\Delta\nu_i$ | Assignment |
|---|---|---|
| | CH$_3$COF | |
| 39612 | −299 | $15^0_3$ (*E*) |
| 39690 | −222 | $15^0_2$ (*E*) |
| 39696 | −216 | $15^0_2$ ($A_1$) |
| 39796 | −115 | $15^0_1$ (*E*) |
| 39864 | −48 | $15^1_2$ (*E*) |
| 39912 | 0 | $15^0_0$ ($A_1$, *E*) |
| 39964 | 52 | $15^1_1$ ($A_2$, *E*) |
| 40077 | 165 | $15^1_0$ (*E*) |
| 40207 | 295 | $15^2_0$ ($A_1$, *E*) |
| 40311 | 399 | $15^3_0$ (*E*) |
| | CD$_3$COF | |
| 39724 | −180 | $15^0_2$ ($A_1$, *E*) |
| 39810 | −94 | $15^0_1$ (*E*) |
| 39861 | −43 | $15^1_2$ (*E*) |
| 39904 | 0 | $15^0_0$ ($A_1$, *E*) |
| 39945 | 41 | $15^1_1$ ($A_2$, *E*) |
| 39991 | 87 | $15^2_2$ ($A_1$, *E*) |
| 40039 | 135 | $15^1_0$ (*E*) |
| 40113 | 209 | $15^3_2$ (*E*) |
| 40169 | 265 | $15^2_0$ ($A_1$, *E*) |
| 40201 | 297 | $15^3_1$ (*E*) |
| 40223 | 319 | $15^4_2$ ($A_1$, *E*) |

*Note*: Vibronic transitions designation: $15^{v'}_{v''}$, where 15 is the number of torsion vibration,[7,8] $v'$ and $v''$ are the vibrational quantum numbers in the $S_0$ and $S_1$ states, respectively. Futhermore, the symmetry classification by $A_1$, $A_2$, and E types is presented for torsion levels. The selection rules for optical transitions among them are $A_1 \leftrightarrow A_1$, $A_2 \leftrightarrow A_2$, and $E \leftrightarrow E$. It was shown that for the molecules with CH$_3$ and CD$_3$ tops the intensity ratios for $A_1 \leftrightarrow A_1$ and $E \leftrightarrow E$ transitions are 2 : 1 and 7 : 8, respectively.

**Table 2**. Assignment of "pseudoorigins" in the UV spectra of AF-$h_3$ and AF-$d_3$ molecules (cm$^{-1}$)

| $\nu_i$ | $\Delta\nu_i$ | Assignment |
|---|---|---|
| | $CH_3COF$ | |
| 38483 | −1489 | $14^{5+}_{6}$ |
| 38514 | −1398 | $14^{2\pm}_{4}$ |
| 38695 | −1217 | $14^{4+}_{5}$ |
| 38776 | −1136 | $14^{0\pm}_{2}$ |
| 38991 | −921 | $14^{5+}_{5}$ |
| 39270 | −642 | $14^{4+}_{4}$ |
| 39343 | −569 | $14^{0\pm}_{1}$ |
| 39561 | −351 | $14^{5+}_{4}$ |
| 39647 | −265 | $14^{2\pm}_{2}$ |
| 39793 | −119 | $14^{1\pm}_{1}$ |
| 39912 | 0 | $0^0_0$ ($14^{0\pm}_{0}$) |
| 40217 | 305 | $7^1_0\,9^0_1$, $14^{2\pm}_{1}$ |
| 40263 | 351 | $10^1_0$ |
| 40361 | 449 | $14^{1\pm}_{0}$ |
| 40616 | 704 | $10^2_0$ |
| 40676 | 764 | $8^1_0$ |
| 41072 | 1160 | $6^1_0$ |
| 41134 | 1222 | $3^1_0$ |
| 41431 | 1519 | $3^1_0\,7^1_0\,9^0_1$, $8^2_0$ |
| 41484 | 1572 | $3^1_0\,10^1_0$ |
| 41881 | 1969 | $3^1_0\,8^1_0$ |
| 42285 | 2373 | $3^1_0\,6^1_0$ |
| 42349 | 2437 | $3^2_0$ |
| | $CD_3COF$ | |
| 37830 | −2074 | $5^0_1\,7^0_3\,9^4_0$ |
| 38275 | −1629 | $5^0_1\,7^0_2\,9^3_0$ |
| 38352 | −1552 | $14^{1\pm}_{4}$ |
| 38583 | −1321 | $7^0_3\,9^3_0$ |
| 38708 | −1196 | $5^0_1\,7^0_1\,9^2_0$ |
| 38740 | −1164 | $14^{2\pm}_{4}$ |
| 38844 | −1060 | $14^{1\pm}_{3}$ |
| 39025 | −879 | $7^0_2\,9^2_0$ |
| 39128 | −776 | $14^{3\pm}_{4}$ |
| 39156 | −748 | $5^0_1\,9^1_0$ |
| 39238 | −666 | $14^{2\pm}_{3}$ |
| 39336 | −568 | $14^{1\pm}_{2}$ |
| 39411 | −493 | $14^{0\pm}_{1}$ |
| 39467 | −437 | $7^0_1\,9^1_0$ |
| 39488 | −416 | $14^{4+}_{4}$ |
| 39496 | −408 | $14^{4-}_{4}$ |
| 39904 | 0 | $0^0_0$ ($14^{0\pm}_{0}$) |
| 40120 | 216 | $14^{3\pm}_{2}$ |
| 40336 | 432 | $7^1_0\,9^0_1$ |
| 40481 | 577 | $14^{4-}_{2}$ |
| 40704 | 800 | $9^2_0$ |
| 41132 | 1228 | $3^1_0$ |
| 41562 | 1658 | $3^1_0\,7^1_0\,9^0_1$ |

*Note*: The numbering of vibrational modes follows Refs. 7 and 8, "+" and "−" signs correspond to the inversion splitting of energy levels in the $S_1$ states, see text.

tions in AF-$h_3$ and AF-$d_3$ are associated with the groups of most intense and clear bands, which are depicted in Table 1. Hence, these arguments support the assignment 39912 and 39904 cm$^{-1}$ bands with weak intensity to the origins of the $S_1 \leftarrow S_0$ transitions in the AF-$h_3$ and AF-$d_3$ molecules. Other characteristic groups in the spectra of these molecules accompany the "pseudoorigins" listed in Table 2 with assignments.

Our assignment of the $S_1 \leftarrow S_0$ transition origins in the AF-$h_3$ and AF-$d_3$ molecules is supported by the observation of the following intervals between origins and "pseudoorigins": −569, +1222, and 2·(+1222) cm$^{-1}$ for AF-$h_3$ and +1228 cm$^{-1}$ for AF-$d_3$ molecule. The interval −569 cm$^{-1}$ coincides with the −567 cm$^{-1}$ frequency of nonplanar "inversion" vibration of C=O fragment determined from the vibrational spectra of the AF-$h_3$ molecule in the $S_0$ state,[8] whereas the other intervals certainly correspond to the fundamental and overtone frequencies of stretching C=O vibrations in the $S_1$ state. Moreover, the assignments of origins of electronic transitions in AF-$h_3$ and AF-$d_3$ given above provide good correspondence with the analogous values in the series of other molecules, *c.f.* formaldehyde-$h_2$ and -$d_1$ (28188 and 28244 cm$^{-1}$),[11] formyl fluoride-$h_1$ and -$d_1$ (37488 and 37504 cm$^{-1}$),[12,13] acetaldehyde-$h_4$ and -$d_4$ (29771 and 29756 cm$^{-1}$).[15]

It should be noted that the characteristic feature of the vibronic spectra of both AF-$h_3$ and AF-$d_3$ molecules is the manifestation of a significant number of "pseudoorigins" shifted from the origins toward the lower frequency (on the wavenumber scale) by the intervals that do not match the fundamental frequencies determined by vibrational spectroscopy. Many of these "pseudoorigins" are separated by the distances of multiples of the frequencies of nonplanar C=O vibrations in the $S_0$ states (569 and 492 cm$^{-1}$ for AF-$h_3$ and AF-$d_3$, respectively). Using this fact and excluding the possibility of impurities in the samples under study (see experimental part)*, we attribute these "pseudoorigins" to the hot transitions between inversion levels of the $S_1$ and $S_0$ electronic states. Analysis of possible "pseudoorigin" assignments allows us to find the unique ones for each AF-$h_3$ and AF-$d_3$ molecule, which, on the one hand, involve all the observed "pseudoorigins" of the particular type and, on the other hand, yield reasonable potential functions for inversion (see below). These assignments are presented in Table 2.

Furthermore, the "pseudoorigins" are observed in the low-frequency region of AF-$d_3$ spectrum. They form two series of intervals with respect to the origin of electronic transition: a) −437, −879, −1321 cm$^{-1}$ and b) −748, −1196, −1629, −2074 cm$^{-1}$, so that the latter series is shifted from the former by 310 cm$^{-1}$ toward the lower frequencies. These intervals also do not match the fundamental frequencies of the AF-$d_3$ molecule in the $S_0$ state, and the corresponding "pseudoorigins" can be assigned only to the combination transitions. The interval of 310 cm$^{-1}$ may be interpreted as the difference between AF-$d_3$ fundamental frequencies in the $S_0$ states, namely, $\upsilon''_5 - \upsilon''_7$,[7,8] so we tentatively assign the "pseudoorigins" forming the above sequences of intervals to the $7^0_{\upsilon''}9^{\upsilon'}_0$ and $5^0_1 7^0_{\upsilon''-1} 9^{\upsilon'}_0$ ($\upsilon' = \upsilon''$) transitions, see Table 2.

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* The "pseudoorigins" described above were also observed in the vibronic spectra recorded using light filters transparent only for sufficiently long-wave radiation. This rules out attributing the "pseudoorigins" to products of the photochemical decomposition of AF molecules.

**Table 3**. Some fundamental frequencies of AF-$h_3$ and AF-$d_3$ molecules in the $S_0$ and $S_1$ states ($cm^{-1}$)

| Molecule | Electronic state | Form, number and symmetry of vibrational mode[7] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\nu_3$ ($\nu$CO) *a'* | $\nu_6$ ($\nu$C—C) *a'* | $\nu_7$ ($\omega CH_3$) *a'* | $\nu_8$ ($\nu$C—F) *a'* | $\nu_9$ ($\delta$CCO) *a'* | $\nu_{10}$ ($\delta$CCF) *a'* | $\nu_{14}$ ($\gamma$C=O) *a''* | $\nu_{15}$ ($\tau CH_3$) *a''* |
| $CH_3COF$ | $S_0$[7, 8] | 1870 | 1188 | 1000 | 826 | 598 | 428 | 567 | 115** |
| | $S_1$ | 1222 | 1160 | 903* | 764 | — | 351 | 449 | 165 |
| $CD_3COF$ | $S_0$[7, 8] | 1869 | 1204 | 839 | 778 | 575 | 395 | 491 | 94** |
| | $S_1$ | 1228 | — | 1007* | — | 401* | — | 416 | 135 |

* Determined from the combination transition.

** This work.

In the high frequency region of the spectra of AF-$h_3$ and AF-$d_3$ the following intervals (from the origins of electronic transitions) are found: 305, 351, 764, and 1160 $cm^{-1}$ for AF-$h_3$ and 800 $cm^{-1}$ AF-$d_3$. The assignments of the corresponding "pseudoorigins" are also given in Table 2. Table 3 contains some of the fundamental frequencies of AF-$h_3$ and AF-$d_3$ molecules in the $S_1$ and $S_0$ states. It should be noted that despite the complexity and apparent ambiguity in the above assignments of several "pseudoorigins" in the spectra of the AF-$h_3$ and AF-$d_3$ molecules, it is difficult to guess reasonable alternatives to them.

In order to estimate the geometric parameters of AF molecules in the $S_1$ state, we performed a simulation of the rotational contour of the band corresponding to the origin of electronic transition in AF-$h_3$ molecule using a program similar to that described elsewhere.[22] The geometry of this molecule in the $S_0$ state was taken from the microwave study.[6] Taking into account the relations between geometric parameters of formyl fluoride molecule in the $S_1$ and $S_0$ states[12,23] and activity of the particular vibrations in the vibronic spectrum of AF-$h_3$ molecule obtained here (according to the Franck-Condon principle, equilibrium values of corresponding internal coordinates may differ markedly in the $S_1$ and $S_0$ states), we exploited different possibilities varying the following parameters of AF-$h_3$ molecule in the $S_1$ state:

a) internuclear *r*(C=O), *r*(C—C), and *r*(C—F) distances; b) planar CCF angle; c) nonplanar angle $\theta$ corresponding to the deviation of C=O bond from the CCF plane.

The best agreement of calculated and observed rotational contours of the AF-$h_3$ vibronic bands was attained with elongation of the internuclear distance in the $S_1$ state by 0.18 Å with respect to that in the $S_0$ state, and a value of $\theta$ angle equal to 45°. For these parameters the band under study has a hybrid character belonging to the (A+B+C) type (see Fig. 3). This result deserves more detailed considerations.

Since in the equilibrium configuration of AF molecule in the $S_1$ state the oxygen atom may deviate from the CCF plane by the angle $\theta$ in both sides, the potential function for inversion has two minima separated by the

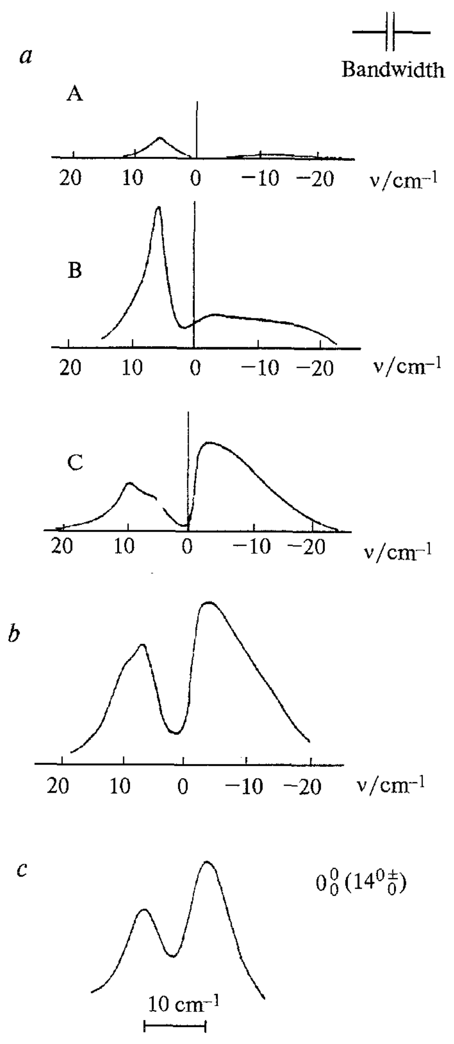

**Fig. 3.** Calculated and measured rotational contours of vibronic bands of AF-$h_3$ molecule: *a* — calculated contours for the bands of A, B, and C types; *b* — calculated contours for the bands of hybrid (A+B+C) type (contribution from A-type is small, B : C = 2 : 5); *c* — experimentally observed contour of $0^0_0(14^{0+}_0)$ band. The following rotational constants were used in the calculations: $A'' = 0.3680$, $B'' = 0.3247$, $C'' = 0.1783$ $cm^{-1}$ for the $S_1$ state; $T = 300$ K.

**Table 4**. Energies of inversion vibrational levels ($cm^{-1}$) and parameters of potential functions for inversion of AF-$h_3$ and AF-$d_3$ molecules in the $S_1$ states

| Level | $CH_3COF$ | | $CD_3COF$ | | Potential parameters (4) | $CH_3COF$ | $CD_3COF$ |
|---|---|---|---|---|---|---|---|
| | Experiment | Calculation | Experiment | Calculation | | | |
| 0− | — | 0,001 | — | 0.00 | $K_1/cm^{-1}$ Å$^{-2}$ | 1263.6 | 1016.5 |
| 1+ | 449 | 448.0 | 416 | 414.3 | | | |
| 1− | 449 | 448.0 | 416 | 414.3 | $k_1/cm^{-1}$ | 3900.9 | 4107.9 |
| 2+ | 874 | 874.4 | 810 | 812.1 | | | |
| 2− | 874 | 874.7 | 810 | 812.1 | $k_2$/Å$^{-2}$ | 1.95 | 1.72 |
| 3+ | — | 1274.8 | 1192 | 1192.8 | | | |
| 3− | — | 1278.8 | — | 1193.1 | $V_0/cm^{-1}$ | 2090 | 2370 |
| 4+ | 1630 | 1629.8 | 1552 | 1553.5 | | | |
| 4− | — | 1661.7 | 1560 | 1556.3 | $\theta_m$/deg | 41 | 45 |
| 5+ | 1921 | 1920.6 | — | 1881.5 | | | |

barrier corresponding to the planar configuration of CCOF fragment. In one-dimensional approximation such a potential function may be represented as

$$V(Z) = K_1Z^2 + k_1\exp(-k_2Z^2), \qquad (4)$$

where $Z$ is the deviation of the oxygen atom from the CCF plane. All inversion levels in this potential are either doubly degenerated if the potential barrier is high, or split if the potential barrier is not too high and the degeneracy is lifted.

The AF molecule in the $S_0$ state belongs to the point symmetry group $C_s$, whereas in the $S_1$ state it belongs to the $G_2$ molecular symmetry group (if the torsion splitting is not taken into account[24]), which is isomorphous to the $C_s$ point group. Hence, the bands of the vibronic transitions between the vibrational levels of the same and different symmetries must be of different types.

It is known that for "pure" electronic $S_1 \leftarrow S_0$ transitions in the molecules of carbonyl compounds, which have the symmetry plane in the $S_0$ states, the vectors of transition dipole moment are normal to this plane and corresponding transitions are of $\tilde{A}\,^1A'' \leftarrow \tilde{X}\,^1A'$ type (as, for example, in the acetaldehyde[15] and formyl fluoride[12] molecules). Therefore, if one designates lower and upper (in energy) components of the split inversion levels as "+" and "−", respectively, then for the $S_1 \leftarrow S_0$ electronic transition in AF molecule, a C-type band (principal inertia axis C is perpendicular to the symmetry plane) should correspond to the $14^{0+}{}_0$ vibronic transition, whereas a hybrid (A+B)-type band should correspond to the $14^{0-}{}_0$ vibronic transition. If, however, the splitting of $0^+$ and $0^-$ components of zeroth vibrational level is large enough to be observed under experimental conditions, the bands of $14^{0+}{}_0$ and $14^{0-}{}_0$ transition must coincide so that the band corresponding to the origin of electronic transition should look like a hybrid (A+B+C)-type band. Obviously, exactly the same picture is observed for the AF molecule, whereupon the contribution from an A-type band is very small and practically unobservable and the intensity of the $14^{0+}{}_0$ band is approximately twice as large as that of the $14^{0-}{}_0$ band (see Fig. 3).

The assignment of several bands to the inversion transitions of AF-$h_3$ and AF-$d_3$ molecules (Table 2) allows us to calculate the energies of inversion levels of these molecules in the $S_1$ state and determine the corresponding potential functions of inversion (4). These calculation were carried out using a program similar to that described in Ref. 25. Table 4 lists the observed and calculated energies of inversion levels, the parameters $K_1$, $k_1$, and $k_2$ in equation (4), the heights of potential barrier $V_0$, and the equilibrium θ values $\theta_m$ for AF-$h_3$ and AF-$d_3$ molecules. These data show that:

1) the heights of potential barriers to inversion $V_0$ and equilibrium angles $\theta_m$ calculated independently for AF-$h_3$ and AF-$d_3$ molecules agree well indicating the relatively good separation of vibrations from other internal motions of AF-$h_3$ and AF-$d_3$ molecules in the $S_1$ state;

2) the $V_0$ values calculated for AF-$h_3$ and AF-$d_3$ molecules are consistent with the analogous value obtained for formyl fluoride molecule (250 $cm^{-1}$)[13], whereas the $\theta_m$ value agrees well with equilibrium angle 45° deduced from the rotational contour simulations for the $0^0{}_0(14^0{}_0)$ band of AF-$h_3$ molecule;

3) the very small inversion splitting of the zero vibrational level $(0^-)$—$(0^+)$ is in line with the hybrid type of the contour of the 39912 $cm^{-1}$ band (assigned to the origin of electronic transition) in the spectrum of the AF-$h_3$ molecule.

Figure 4 depicts the potential functions of inversion obtained as described above for the AF-$h_3$ molecule in the $S_1$ and $S_0$ states (for the latter, harmonic approximation is used) and experimentally observed transitions between inversion levels of the $S_1$ and $S_0$ states. Evidently, the hot transitions even from rather high inversion levels manifest themselves in the spectrum despite their very low populations. We have shown[23] that this effect originates from the high probability of such transitions.

**Table 5.** Parameters of potential functions for internal rotation and energies of torsion vibrational levels of AF-$h_3$ and AF-$d_3$ molecules in the $S_0$ and $S_1$ states ($cm^{-1}$)

| Molecule | Electronic state | Method | $1E_1$ | $2A_1$ | $2E$ | $3E$ | Parameter | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | $F$ | $V_3$ | $V_3/V_6$ |
| $CH_3COF$ | $S_0$ | e | 115 | 216 | 222 | 299.5 | 5.65 | | |
| | | c | 120.7 | 218.7 | 226.2 | 294.5 | | 360 | |
| | | c | 115.3 | 215.8 | 222.1 | 297.2 | | | 371/−20 |
| | $S_1$ | e | 165 | 295 | | 399 | 5.62 | | |
| | | c | 154.3 | 291.3 | 293.0 | 404.5 | | 560 | |
| | | c | 162.3 | 297.5 | 300.1 | 398.2 | | | 523/38 |
| $CD_3COF$ | $S_0$ | e | 94 | 180 | | | 3.03 | | |
| | | c | 94.2 | 179.9 | 180.2 | 254.4 | | 380 | |
| | | c | 94.0 | 180.0 | 180.3 | 255.4 | | | 384/3 |
| | $S_1$ | e | 135 | 265 | | 389 | 2.99 | | |
| | | c | 137.1 | 266.5 | 266.5 | 387.4 | | 770 | |
| | | c | 135.0 | 265.0 | 265.0 | 389.0 | | | 826/−28 |

*Note*: For the rotational constants $F = h/8\pi^2 cI_r$ ($I_r$ — reduced inertia moments) the experimental (microwave) geometric parameters for the $S_0$ states[6] and their estimations from the simulations of the rotational contours of vibronic bands for $S_1$ states were used; e — experiment, c — calculation.

Detection of vibronic transitions between torsion levels of AF-$h_3$ and AF-$d_3$ molecules in the $S_1$ and $S_0$ states (see Table 1) permits us to evaluate the energy of torsion levels. In turn, these data together with geometric parameters of AF molecule make it possible to determine the potential energy functions for internal rotation (1) of AF-$h_3$ and AF-$d_3$ molecules in the $S_1$ and $S_0$ states by a program similar to that described in Ref. 21. Table 5 presents the measured and calculated energies of torsion levels together with the parameters of internal rotation potential functions of AF-$h_3$ and AF-$d_3$ molecules calculated under two approximations, *i.e.*, retaining one ($V_3$) or two ($V_3$ and $V_6$) harmonics in the series (1); in both cases the height of potential barriers is equal to $V_3$ values. It follows from Table 5 that 1) being small by magnitude and different even in sign for isotopically distinct molecules, $V_6$ parameters probably are not physically meaningful*;

2) the heights of potential barriers to internal rotation calculated independently for AF-$h_3$ and AF-$d_3$ molecules are in good agreement for the $S_0$ states but differ markedly for the $S_1$ states; seemingly, this reflects the fact that torsion vibrations are better separated from other vibrations in the $S_0$ states than in the $S_1$;

3) the potential barriers to internal rotation in AF-$h_3$ and AF-$d_3$ molecules are significantly higher in the $S_0$ states than those in the $S_1$ states.

It is worth noting also that the intensity distribution in the vibronic transitions between torsion energy levels of AF-$h_3$ and AF-$d_3$ molecules in the $S_0$ and $S_1$ states (see Fig. 2) indicates that for these molecules the minima on the $S_1$ potential energy surfaces should be shifted

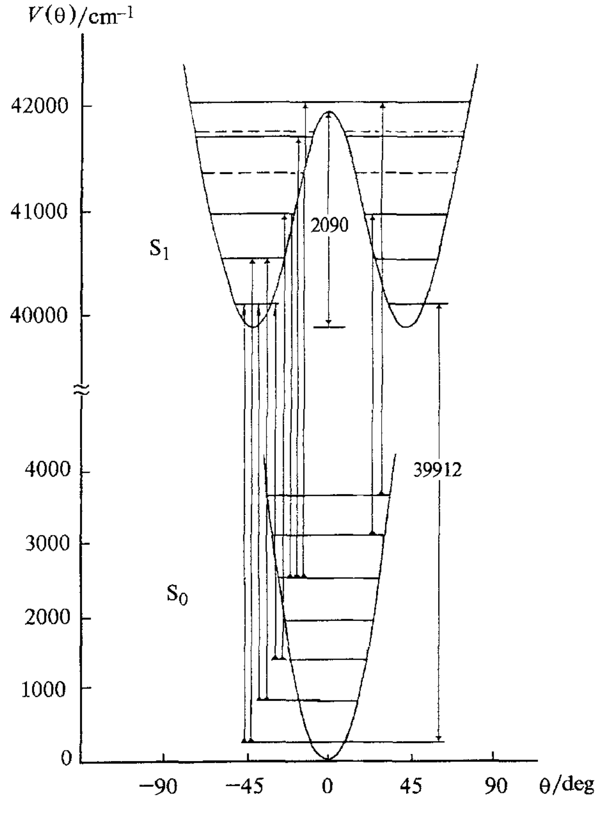

**Fig. 4.** Potential functions for inversion for AF-$h_3$ molecule in the $S_0$ and $S_1$ states and experimentally observed vibronic transitions.

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* Determination of $V_3$ and $V_6$ parameters of the potential function for internal rotation (1) for the acetaldehyde molecule in the $S_0$ state demonstrated that the calculated value of $V_6$ coefficient is physically meaningful only if the variation of geometric parameters of the molecule during internal rotation are taken into account.[26]

relative to those on the $S_0$ surfaces along the torsion coordinate, as in the case for acetaldehyde[15,16] and acetone[3,16,17] molecules.

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