Reviews

Application of vibronic spectroscopy to conformational analysis. Investigations of molecules of carbonyl compounds*

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Application of vibronic spectroscopy to the conformational analysis of molecules in the ground and excited electronic states is reviewed. The basic concepts of the method as well as its methodological and technical aspects are discussed. The abilities of vibronic spectroscopy are exemplified by the results obtained for molecules of carbonyl compounds.

Key words: vibronic spectroscopy; carbonyl compounds, molecular structure, conformational analysis.

For many years, the wide use of vibronic spectroscopy for studying the structure of complex polyatomic molecules and, in particular, conformational analysis, has been limited by at least two factors. First, analysis of the vibrational structure of electronic transitions in polyatomic molecule spectra is very laborious. Second, the gas-phase electronic spectra of complex polyatomic molecules at room temperature do not exhibit clear vibrational patterns due to overlapping of the vibronic bands. However, the supersonic inert gas jet technique developed in the past 15 years has significantly extended the abilities of vibronic spectroscopy.

Below we will consider briefly the supersonic jet technique, but first we will discuss the basic aspects of conformational analysis by means of vibronic spectroscopy common to spectra recorded by any procedure under any conditions. The possibilities of this method will be illustrated for molecules of carbonyl compounds.

It should be noted that for many relatively complex molecules it is still possible to obtain gas-phase vibronic spectra at room temperature. Although there are a great number of vibrational levels in these molecules in both the ground and excited electronic states, by no means are all of the transitions between them observed in the spectra. First, some of the transitions may be forbidden by the symmetry selection rules. Second, the "hot" transitions from high vibrational levels of the ground electronic state are not observed, as a rule, due to their negligible populations. Third, the Franck—Condon principle* plays an important role as follows:

1. If the equilibrium values of some internal coordinate of a molecule are close in both ground and excited

* The review is based on a report at the Vibrational Spectroscopy Conference dedicated to the 80th birthday of B. I. Stepanov (Minsk, Belarus', October 3—5, 1993).

* We assume the formulation of the Franck—Condon principle that does not exclude dependence of the electronic transition moment of a molecule on the displacements of nuclei.[1]

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electronic states, the sequence bands 0—0, 1—1, 2—2, *etc.* are the most intense among the transitions between the corresponding vibrational levels. As a rule, these bands rapidly decrease in intensity and appear in the spectrum as groups near the origin of the electronic transition (*i.e.*, the transition between zero-point vibrational levels of ground and excited electronic states denoted as 0^0_0) and the pseudo-origins ($N_0^{v'}$, $N_{v''}^0$, $N_0^{v'}M_0^{v'}$, *etc.*, where N, M designate the vibrational degrees of freedom and v', v'' are the vibrational quantum numbers of the excited and ground electronic states, respectively) or nearly coincide with them.

2. If the equilibrium values of some internal coordinate of a molecule are essentially different in the ground and excited electronic states, the progression bands 0—1, 0—2, *etc.* are the most intense and the first progression members (0^0_0 band, for instance) may not manifest themself due to very low intensity.

Figure 1 shows the fragment of the gas-phase vibronic spectrum of cyclopropanecarboxaldehyde () in the $S_1 \leftarrow S_0$ transition region (S_0 and S_1 are the ground and first excited singlet electronic states, respectively).[2] In the gas phase at room temperature, *cis*- and *trans*-conformers of this molecule exist. The minima corresponding to the conformers on the S_1 potential energy surface are only slightly shifted from those on the S_0 surface, so among the *trans*-cyclopropanecarboxaldehyde vibronic transitions the 0^0_0 band is the strongest (see Fig. 1). The sequence bands with rapidly decreasing intensities are superimposed on this band on the left- and right-hand sides. The 0^0_0 band of *cis*-cyclopropanecarboxaldehyde also has the highest intensity of the vibronic bands associated with this conformer (the intense bands on both sides of it belong to the *trans*-conformer).

Figure 2 shows the fragments of the vibronic spectrum of the acetophenone ($C_6H_5COCH_3$) molecule in the $T_1 \leftarrow S_0$ and $S_1 \leftarrow S_0$ electronic transition regions (T_1 is the first excited triplet electronic state).[3] It is evident from Fig. 2 that the relative intensities of the vibronic bands for these transitions are essentially different: the strongest band of the $T_1 \leftarrow S_0$ spectrum corresponds to the 0^0_0 transition, whereas for the $S_1 \leftarrow S_0$ spectrum the transitions into the torsional levels of the methyl top in the S_1 state have the highest strengths. The adjustment of the calculated (using Franck—Condon factors) band intensities to the measured ones for the torsional transitions $t_0^{v'}$ of the methyl top[3] reveals that the potential minima of the acetophenone molecule in the S_0 and T_1 states correspond to essentially the same internal rotation angles, while the potential minima in the S_1 state are significantly displaced along this coordinate (by approximately 60°).

The above examples clearly illustrate that the Franck—Condon principle not only simplifies the molecular vibronic spectra, but also discriminates between the internal coordinates having similar and essentially different equilibrium values in the ground and excited electronic states. If it is possible to experimentally record the vibronic bands sufficiently clearly, the geometric parameters of the conformers in the excited electronic states may be estimated by calculating not only the relative band intensities (as for the acetophenone molecule), but also the rotational contours of the vibronic bands. To do this the geometric parameters of the conformers in the ground electronic state must be known. Then, some of the geometric parameters of the conformers in excited electronic states should be varied until the calculated rotational contour (envelope) provides the best fit to the experimental ones. This problem (like simulations of relative band intensities), does not in general have a single solution, but it may nevertheless be solved providing close analogies or additional information (such as the activity of some vibrations in the vibronic spectrum) exists.

Figure 3 illustrates the simulations of the vibronic band rotational contours for *cis*- and *trans*-conformers of the cyclopropanecarboxaldehyde molecule. The A, B, and C-type bands (in the calculations, the dipole moments of the conformers varied along the *a*, *b*, and *c*

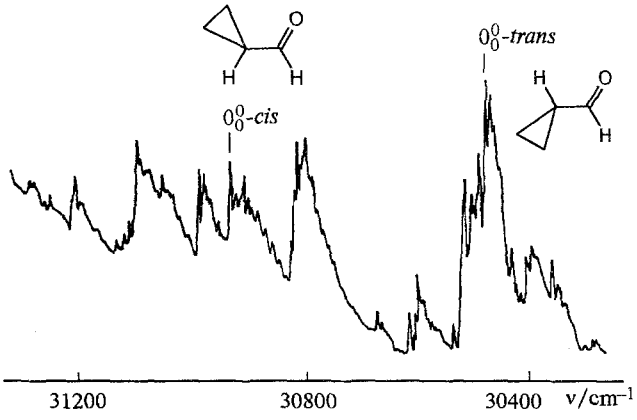

Fig. 1. The fragment of the vibronic spectrum of cyclopropanecarboxaldehyde molecule in the $S_1 \leftarrow S_0$ transition region.[2]

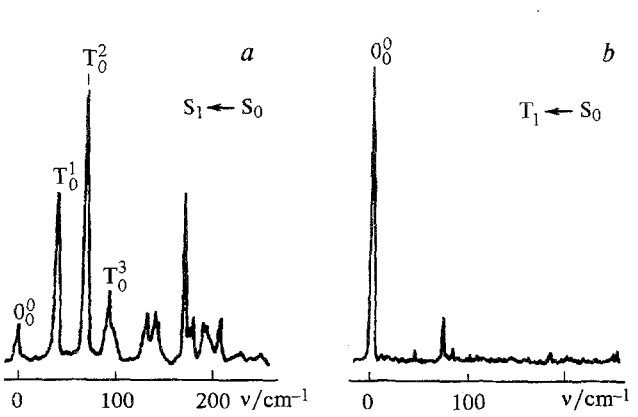

Fig. 2. The $S_1 \leftarrow S_0$ (*a*) and $T_1 \leftarrow S_0$ (*b*) fragments of the vibronic transition spectra of the acetophenone molecule.[3]

principle axes of inertia, respectively) were simulated by lengthening the C=O bond in the S_1 state by 0.1 Å with respect to that in the S_0 state for both conformers and shortening the central C—C bond by 0.1 Å for the *trans*-conformer. It should be noted that some of the other conformer parameters were also varied in these calculations using analogies with formaldehyde, acetaldehyde, acroleine, and glyoxal molecules for which the estimations of the S_1 geometric parameters are already known. It is clear from Fig. 3 that the observed 0^0_0 transition bands of the *cis*- and *trans*-conformers of cyclopropanecarboxaldehyde agree satisfactorily with the calculated C and B-type bands, respectively. The *c* and *b* principle axes are perpendicular to the symmetry planes of the corresponding conformers, therefore the dipole moments of cyclopropanecarboxaldehyde conformers vary in the directions perpendicular to the symmetry planes in the $S_1 \leftarrow S_0$ transitions, the electronic wave functions of the S_1 states are antisymmetric (A") with respect to reflection in the symmetry planes, and the electronic transitions in both conformers belong to the $\tilde{A}^1A'' \leftarrow \tilde{X}^1A'$ type. This example indicates that the simulations of the rotational contour of the vibronic bands allow one not only to estimate the geometric parameters of electroni-

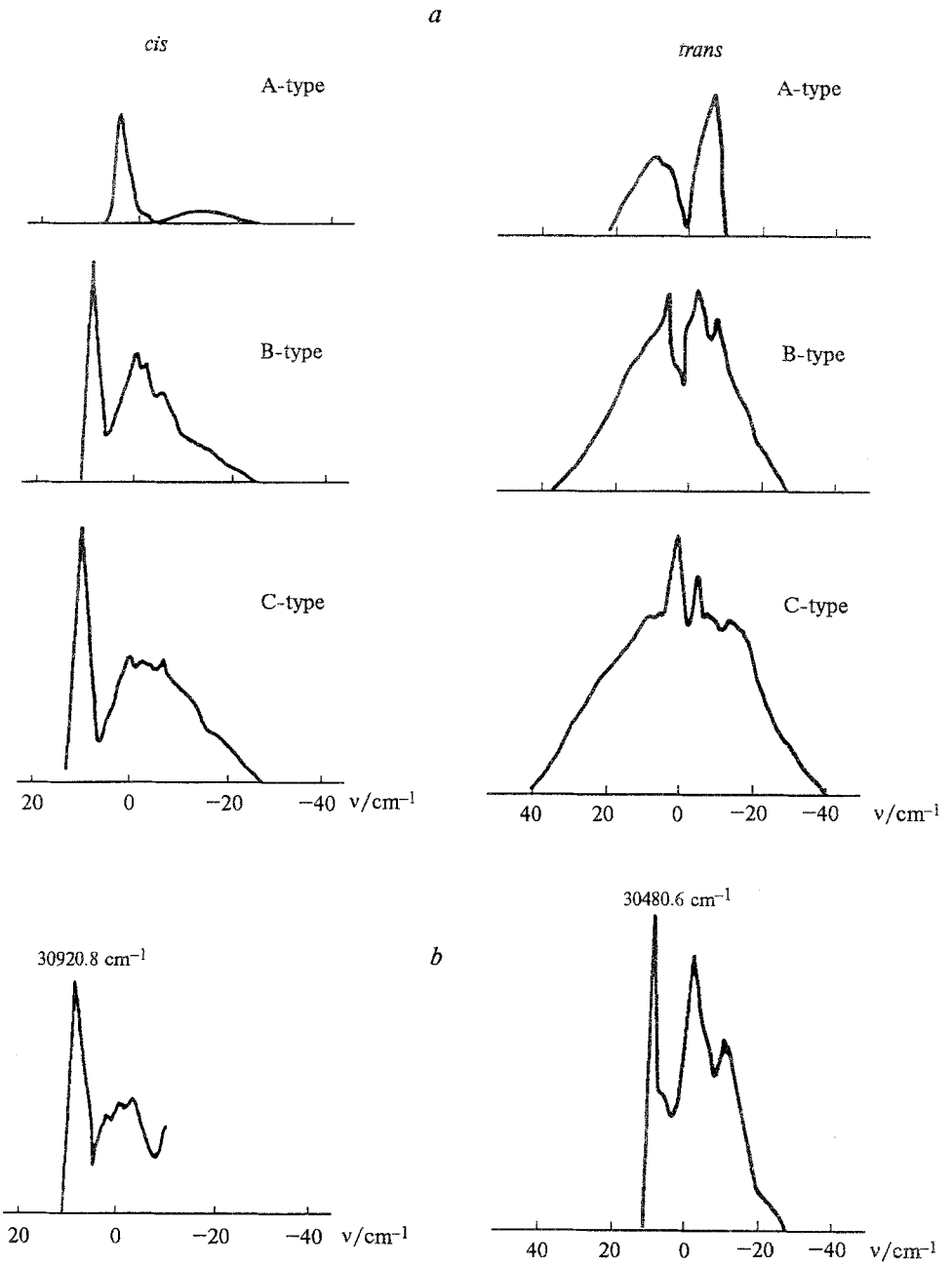

Fig. 3. Rotational contours of the vibronic bands of the cyclopropanecarboxaldehyde conformers: *a*, calculated for A, B, and C types of *cis*- and *trans*-conformers; *b*, experimentally observed 0^0_0 bands.[2]

cally excited conformers, but also to determine the type of symmetry of the corresponding electronic wave functions.

Thus, the analysis of the vibrational structure of electronic transitions in a molecule with internal rotation makes it possible to gain the following data on its molecular structure and conformations:

(i) the energies of the 0^0_0 transitions of the conformers, which correspond to the energies of the excited electronic states relative to the ground state; if the energy difference for the conformers in the ground state is known, then knowing the energy of 0^0_0 transitions one can calculate the energy difference for the conformers in the excited state as well;

(ii) some fundamental frequencies of conformers in the ground and excited electronic states; sometimes it is possible to find systems of energy levels in the spectra associated with some vibrational degrees of freedom, for example, torsions and inversions;

(iii) an estimation of the geometric parameters of the conformers in the excited electronic states *via* calculations of the relative intensities or the rotational contours; in the latter case the symmetry of the electronic wave functions for the electronically excited conformers may also be determined.*

These data permit one to define the potential functions for internal rotation and inversion of the molecule in different electronic states in the following way. The periodic potential function of internal rotation is expanded in the Fourier series

$$V(\varphi) = \sum_n (A_n \cos n\varphi + B_n \sin n\varphi), \qquad (1)$$

where φ is the internal rotation angle.

Potential functions of the inversion of molecules are usually represented as a power series that in addition may (or may not) contain the exponential term

$$V(z) = K_1 z + K_2 z^2 + \ldots + k_1 \exp(-k_2 z^2), \qquad (2)$$

where z denotes the displacement of an atom from the plane.

Further, solving the corresponding one-dimensional Schrödinger equation,[5–7] one seeks the best agreement between the calculated and measured vibrational (torsion or inversion) energy levels. The values of A_n, B_n, K_1, K_2, *etc.* coefficients in expansions (1) and (2) obtained by this iterative procedure determine the form of the corresponding potential function.

Figure 4 shows the potential functions of internal rotation of the cyclopropanecarboxaldehyde molecule in the $S_0(\tilde{X}^1A')$, $T_1(\tilde{a}^1A'')$, and $S_1(\tilde{A}^1A'')$ states obtained by the method described above.[8]

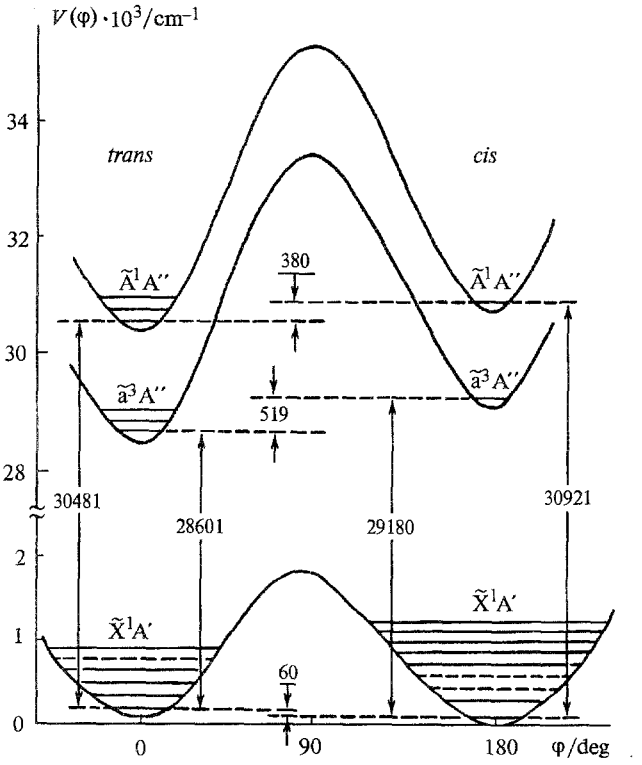

Fig. 4. Potential functions of internal rotation of the cyclopropanecarboxaldehyde molecule in the $S_0(\tilde{X}^1A')$, $T_1(\tilde{a}^3A'')$, and $S_1(\tilde{A}^1A'')$ states.[8]

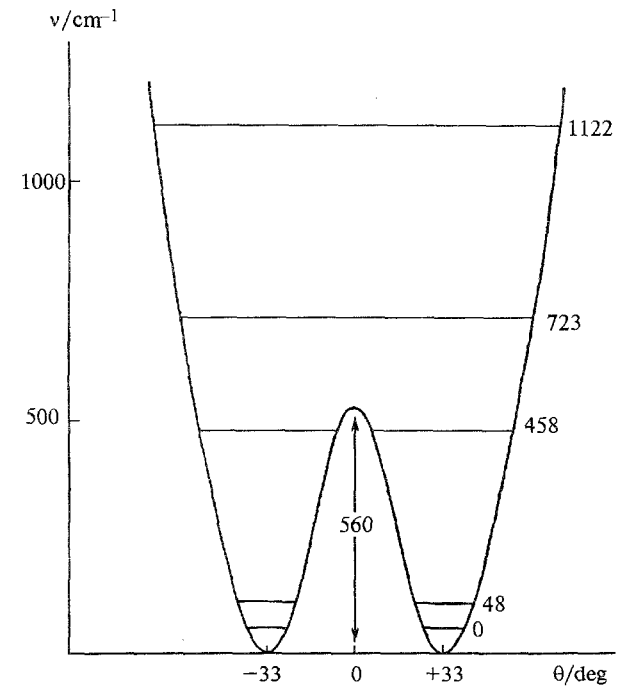

Fig. 5. Potential function of inversion of the *cis*-propanal molecule in the S_1 state; θ is the angle of C—H(aldehyde) bond deviation from the CCO plane.[9]

* No attention is paid here to such problems in the application of vibronic spectroscopy to conformational analysis as the necessity of using nonrigid symmetry groups and accounting for the Dushinsky effect. These issues have been addressed by us previously, see Ref. 4 and references cited therein.

The potential function of inversion of the *cis*-conformer of the propanal molecule in the S_1 state[9] is given in Fig. 5. It is clear from this figure that the *cis*-propanal molecule in the S_1 state has a nonplanar aldehyde fragment (CCOH). In the one-dimensional approximation this may be viewed as the deviation of C—H(aldehyde) bond from a plane by an angle of ~33° (to either side). It is noteworthy that in the *cis*-propanal molecule in the S_0 state the CCOH fragment is planar.

As was stated above, complex polyatomic molecules in the gas phase at room temperature give structureless electronic spectra due to the overlap of the vibronic bands. This problem is eliminated to a considerable extent by cooling the molecules in supersonic inert gas jets.[10—13] This method is based upon fast cooling of the molecules by adiabatic expansion into a vacuum through a narrow nozzle. With sufficient cooling, only the low rotational levels of the lowest vibronic state of a molecule are populated. For this reason, the vibronic bands become much narrower than in the gas phase at room temperature, "hot" transitions are not observed, and the spectrum becomes markedly simpler.

Although there are several examples of usual absorption spectra of molecules cooled using this method,[14,15] the methods of laser spectroscopy are by far more efficient. Nowadays, the most popular techniques for studying molecules in supersonic jets are fluorescence[10—13,16—20] or phosphorescence[21] excitation spectroscopy, and multiphoton ionization spectroscopy.[10,12,13,17—20,22—27] Tunable lasers are used to record all these spectra. Figure 6 schematically illustrates the principles of these methods.

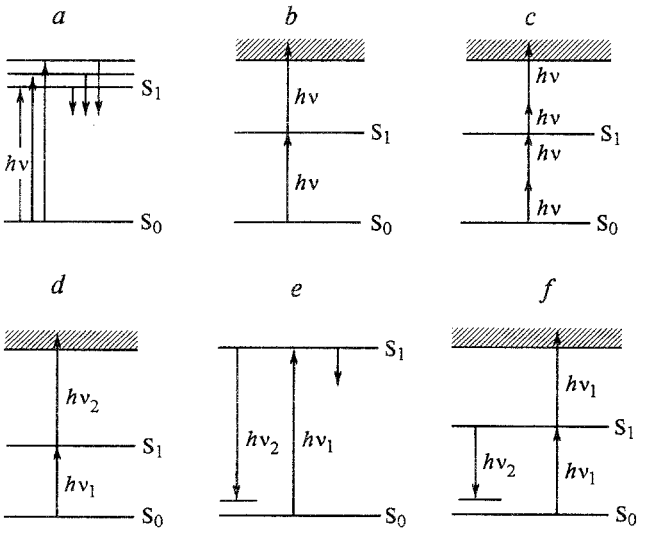

Fig. 6. The principles of laser spectroscopic methods for studying molecules cooled in supersonic jets: *a*, fluorescence excitation spectrum; *b*, one-photon resonance spectrum of two-photon ionization; *c*, two-photon resonance spectrum of four-photon ionization; *d*, two-color multiphoton ionization spectrum ($\nu_1 \neq \nu_2$); *e*, fluorescence dip spectrum; *f*, ionization dip spectrum.

If the energy of the incident photons coincides with the energy difference between the vibrational levels of the ground and excited electronic states of a molecule, then fluorescence is observed (see Fig. 6, *a*); otherwise, weak scattering of the incident photons occurs. Since under the conditions of the supersonic jet only the zero vibrational level of the ground electronic state is populated, one can establish the positions of the vibrational levels of the excited electronic state by continuously varying the photon energy. This spectrum differs from the usual absorption spectrum only in the relative intensities of the vibronic bands. The principle of phosphorescence excitation spectroscopy is the same, but the method meets additional technical difficulties due to the relatively long lifetimes of the molecules in triplet states.

Multiphoton ionization spectroscopy may be employed to investigate weakly fluorescent molecules. Various modifications of the method are shown schematically in Fig. 6, *b—d*. The excitation of a molecule to the vibrational level of an excited electronic state by one (see Fig. 6, *b*) or several (see Fig. 6, *c*) photons is followed by the absorption of the next one or more (see Fig. 6, *b* and *c*, respectively) photons resulting in the ionization of the molecule. Either ions are produced or photoelectrons are detected. Obviously, the ionization of a molecule only occurs if the energy of incident photons coincides with the energy difference between the vibrational levels of the ground and excited electronic states. Gradual variation of photon energy allows one to determine the positions of the vibrational levels in the excited electronic state.

Figure 6, *d* presents the scheme of the so-called "two-color" multiphoton ionization experiment with photons of different frequencies ν_1 and ν_2. The two-color spectroscopy method may be applied to study not only excited states, but also ground electronic states of molecules (the corresponding schemes are given in Fig. 6, *e* and *f*). The first laser with frequency ν_1 is used to obtain the fluorescence excitation (see Fig. 6, *e*) or the multiphoton ionization (see Fig. 6, *f*) spectrum *via* the "intermediate" vibronic state S_1. Then, the second laser with frequency ν_2 induces the radiative decay of the molecules in the "intermediate" state S_1, so the intensity of the fluorescence or ionization caused by the $h\nu_1$ photon of the first laser weakens (dip). This dip occurs only if the $h\nu_2$ photon energy is equal to the energy difference between the intermediate vibronic state S_1 and some vibrational level of the ground electronic state S_0 (see Fig. 6, *e* and *f*). The energies of the vibrational level in the S_0 state may be sequentially determined by tuning the frequency ν_2 of the laser.

Another method suitable for studying molecules with low fluorescence quantum yields due to radiationless $S_1 \rightsquigarrow T_1$ relaxation is sensitized phosphorescence excitation spectroscopy.[28] The essence of this method is the excitation of a molecule to various vibrational levels of the excited S_1 state by a tunable laser and the

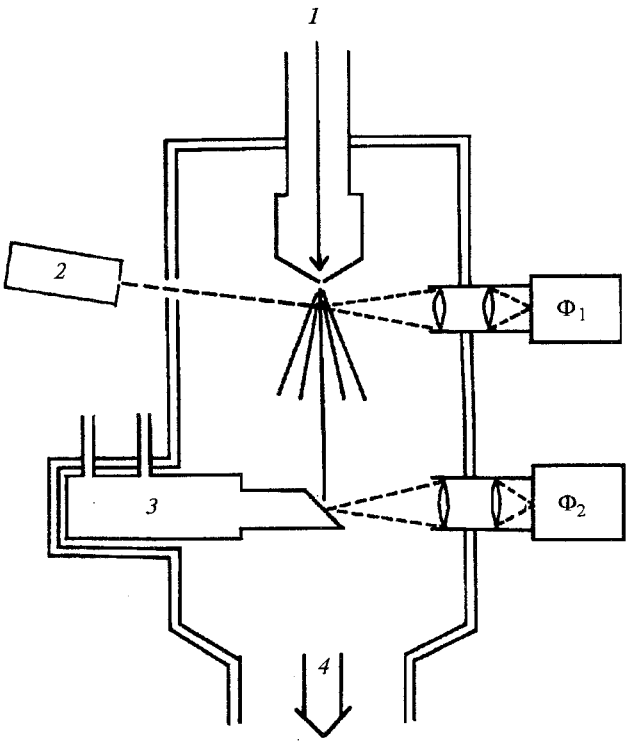

Fig. 7. A scheme of the apparatus for simultaneous registration of the fluorescence (Φ_1) and sensitized phosphorescence (Φ_2) excitation spectra in a supersonic jet:[28] 1, sample; 2, laser; 3, liquid nitrogen; 4, evacuation system.

registration of the phosphorescence from the T_1 state populated by spontaneous $S_1 \rightsquigarrow T_1$ relaxation. It should be emphasized that the sensitized phosphorescence excitation spectrum differs from the $S_1 \leftarrow S_0$ (but not the $T_1 \leftarrow S_0$) absorption spectrum only in the relative intensities of the vibronic bands. Hence, simultaneous registration of the fluorescence and sensitized phosphorescence excitation spectra is especially interesting (Fig. 7). The photomultipliers Φ_1 and Φ_2 detect the fluorescence and sensitized phosphorescence excitation spectra, respectively. Phosphorescence occurs when the molecules reach the substrate cooled by liquid nitrogen; molecules of the substance under study sprayed on the substrate serve as the phosphore. A comparison of the relative intensities of the $S_1 \leftarrow S_0$ vibronic bands in the fluorescence and sensitized phosphorescence excitation spectra allows one to establish the roles of the different vibrational modes in $S_1 \rightsquigarrow T_1$ radiationless relaxation, *i.e.*, to investigate the molecular dynamics.[29]

The methodic and experimental approaches described above permit one to gain important information on molecular structure and conformation. Let us consider the most interesting results for molecules of carbonyl compounds in order to exemplify the abilities of vibronic spectroscopy.*

1. Table 1 summarizes the 0^0_0 ($S_1 \leftarrow S_0$) transition energies, *i.e.*, the relative energies of the S_1 states, for molecules of carbonyl compounds. Clearly, the replacement of the methyl group in the acetaldehyde molecule by more complex alkyl, phenyl, or vinyl groups lowers the S_1 energy, while the replacement by the cyclopropyl group increases the energy of the S_1 states. This result contradicts the Walsh—Hoffmann model,[54] which implies that cyclopropyl and vinyl fragments produce similar effects on molecular properties.

The data presented in Table 1 also indicate that the replacement of the aldehyde hydrogen atom by a methyl group or by a halogen atom increases the energy of the S_1 states.

The cyclic ketones listed in Table 1 have similar S_1 energies (30248—30664 cm^{-1}) except for 2-cyclopentenone (27210 cm^{-1}), which has conjugated double bonds. As one would expect, in this case the S_1 state has lower energy than the S_1 states of parent molecules without conjugated bonds.

2. It is known that molecules of carbonyl compounds have planar —CHO fragments in the S_0 states.[55,56] In S_1 states, some of them retain the planar carbonyl fragments, while in others the carbonyl fragments acquire a pyramidal structure (see Fig. 5). Table 2 lists the heights

* A review of the experimental data on the structural and conformational analyses of carbonyl and dicarbonyl compounds in the ground and excited electronic states will be published elsewhere.[30]

Table 1. Energies ν_{00} (0^0_0) of $S_1 \leftarrow S_0$ transitions in molecules of carbonyl compounds $R^1—CO—R^2$

R^1	R^2	ν_{00}/cm^{-1}	R^1	R^2	ν_{00}/cm^{-1}	R^1	R^2	ν_{00}/cm^{-1}	Molecule	ν_{00}/cm^{-1}
H	H	28188[31]	*cis*-CH_3CH_2	H	29258[38]	*trans*-CH_2=CH	F	34830[45]	Cyclobutanone	30270[50]
F	H	37488[32]	*gauche*-CH_3CH_2	H	28582[39]	*trans*-CH_2=CH	Cl	31350[45]	Cyclopentanone	30264[50]
Cl	H	32755[33]	*cis*-CH_3CH_2	CH_3	30025[40]	*cis*-(*cyclo*-C_3H_5)	H	30921[2]	3-Cyclopentenone	30248[51]
F	F	39252[34]	*trans*-$(CH_3)_2CH$	H	29187[41]	*trans*-(*cyclo*-C_3H_5)	H	30481[2]	2-Cyclopentenone	27210[52]
Cl	Cl	33631[35]	*gauche*-$(CH_3)_2CH$	H	29645[41]	*cis*-(*cyclo*-C_3H_5)	CH_3	31265[46]	2-Indanone	30664[53]
CH_3	H	29771[36]	$(CH_3)_3C$	H	29211[42]	*cis*-(*cyclo*-C_3H_5)	*cis*-(*cyclo*-C_3H_5)	31947[46]		
CH_3	CH_3	30429[37]	*cis*-CH_2=CH	H	24627[43]	C_6H_5	H	26919[47]		
CH_3	F	39912*	*trans*-CH_2=CH	H	25861[43]	C_6H_5	CH_3	27286[3]		
CH_3	Cl	34664*	*trans*-CH_2=CH	CH_3	26121[44]	C_6H_5	F	35687[48,49]		

* This work.

Table 2. The heights of the potential barriers to inversion (V_0/kJ mol^{-1}) of molecules of carbonyl compounds in S_1 states

Molecule	V_0	Molecule	V_0
H_2CO	4.2[31]	$(CD_3)_2CO$	8.3[37]
HDCO	4.2[31]	CH_3COF	25.0*
D_2CO	4.0[31]	CD_3COF	28.4*
HFCO	30.5[32]	CH_3COCl	20.6*
COF_2	98.1[34]	*cis*-CH_3CH_2CHO	6.7[38]
HClCO	19.2[33]	*trans*-$CHOCOCH_3$	1.6[58]
$COCl_2$	37.9[35]	Cyclobutanone	22.1[50]
CH_3CHO	8.2[57]	Cyclopentanone	8.3[50]
CD_3CDO	6.8[57]	3-Cyclopentenone	9.3[51]
$(CH_3)_2CO$	10.1[37]	2-Indanone	12.0[53]

* This work.

of potential barriers to inversion for molecules in the S_1 states determined from experimental data as described above.

Clearly, the successive substitution of hydrogen atom in the formaldehyde molecule by the alkyl groups increases the barrier to inversion, but these changes are not too large. On the other hand, the height of the potential barrier to inversion increases abruptly when the aldehyde hydrogen atoms are replaced by halogens, see Table 2.

It is interesting to note that in the low frequency regions of the gas-phase vibronic spectra of the acetyl halide molecules observed here, namely, CH_3COF, CD_3COF, and CH_3COCl, there are numerous "pseudo-origins", which can be assigned only to complex "hot" transitions between the inversion energy levels of the S_0 and S_1 states. The most surprising fact is that the "pseudoorigins" corresponding to transitions from high inversion levels of the S_0 state are fairly intense despite the very low populations of these levels. Our calculations showed that these "anomalies" reflect the very high probabilities of the corresponding transitions. These results will be published elsewhere in more detail. Here we only present the inversion potential functions and the observed transitions between the inversion levels of the S_0 and S_1 states of the CH_3COF molecule (Fig. 8).

3. As was mentioned above, some of the molecules of carbonyl compounds have planar carbonyl fragments in S_1 states, whereas others have pyramidal carbonyl fragments. Another feature of the molecules of this class, the relative orientation of the substituent in the stable conformers in the ground and lower excited states, allows one to subdivide them into two groups: those with the same orientation and those with the opposite orientation. For instance, for propanal[39] and 2-methylpropanal[41] conformers the potential minima in the S_1 states are virtually not displaced along the internal rotation coordinate of the CHO group relative to those in the S_0 states. In contrast, the potential minima of acetaldehyde[36] and 2,2-dimethylpropanal[42] molecules in the S_0 and S_1 states are strongly shifted from each

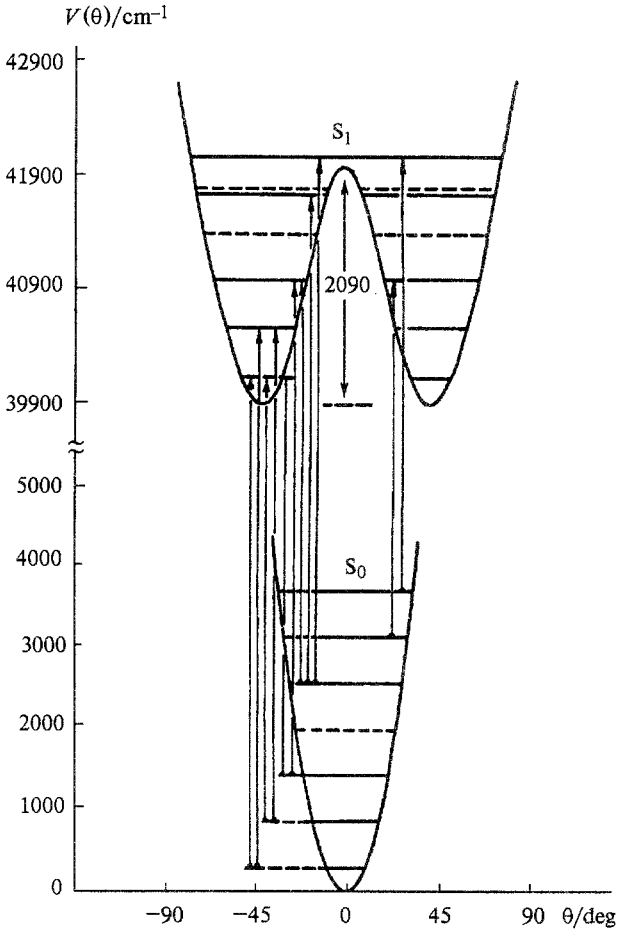

Fig. 8. Potential functions of inversion of the acetyl fluoride molecule in S_0 and S_1 states and the observed transitions between the inversion vibrational energy levels; θ is the angle of deviation of the C=O bond from the CCF plane.

Table 3. The heights of the potential barriers to internal rotation (V_3/kJ mol^{-1}) of molecules of carbonyl compounds with methyl substituents in the S_0 and S_1 states

Molecule	V_3		Molecule	V_3	
	S_0	S_1		S_0	S_1
CH_3CHO	4.8[59] 4.8[57]	7.9[36]	CH_3COF	4.4[61] 4.3*	6.7*
CD_3CDO	4.5[57]	8.0[36]	CD_3COF	4.5*	9.2*
$(CH_3)_2CO$	3.5[60]	8.5[37]	CH_3COCl	5.4[62]	6.2*
$(CD_3)_2CO$	3.5[60]	8.5[37]	CD_3COCl	5.9*	8.3*

* This work.

other along the coordinate of the internal rotation of the CHO group.

Table 3 lists the heights of the potential barriers to internal rotation for the S_0 and S_1 states of a series of molecules with methyl substituents, and Table 4 contains the extreme values of the internal rotation poten-

Table 4. The extreme values of the potential functions of internal rotation of RCHO molecules in the S_0 and S_1 electronic states

R	Conformers and transitions between them	Value of potential function	
		S_0	S_1
CH_3CH_2[39]	*cis*	0	3.3
	cis→gauche	12.7	43.3
	gauche	5.1	0
	gauche↔gauche	6.5	10.5
$(CH_3)_2CH$[41]	*trans*	2.6	0
	trans←gauche	5.5	15.3
	gauche	0	2.6
	gauche↔gauche	7.0	25.2
C_6H_5[63]		19.3	31.2
$CH_2=CH$[63]	*trans*	0	7.8
	trans→cis	26.7	63.6
	cis	7.0	0
cyclo-C_3H_5[63]	*trans*	0.7	0
	trans→cis	21.1	60.2
	cis	0	4.5

Note: For $R=C_6H_5$, the potential barrier corresponds to the conformation in which the planes of the phenyl and aldehyde groups are mutually perpendicular.

tial functions (*i.e.*, the differences between the energies of the conformers and of the barriers to conformational transition) for molecules with less symmetric substituents. The data of Tables 3 and 4 indicate that the barriers to internal rotation in the S_1 states are remarkably higher than those in the S_0 states. This conclusion holds for all of the molecules of carbonyl compounds studied except for benzophenone, for which the torsion vibrational frequencies in the S_0 and S_1 states are likely similar.[40,64] This conclusion is also not true for the potential barriers to internal rotation of the methyl tops in some (but not all) molecules of ketones, where the opposite relation between the barrier heights in the S_0 and S_1 states was observed.[65]

The data of Table 4 also reveal that the stability of the conformers in the S_0 states is the opposite of that in the S_1 states, *i.e.*, the conformer that is the most stable in the S_0 state is the least stable in the S_1 state.

The characteristics of the structure and conformation of molecules of carbonyl compounds strongly influence their properties and dynamic behavior. Obtaining, accumulating, and analyzing these data are essential for correctly understanding and predicting the properties and processes, particularly the photophysical and photochemical properties, of these molecules. As was demonstrated above, vibronic spectroscopy is an efficient tool for conformational analysis that provides structural data for molecules in different electronic states.

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