DOES INTERNAL CONVERSION RESULT IN THE STATISTICAL REDISTRIBUTION OF ENERGY?

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ABSTRACT

Following a brief review of previous experimental and theoretical studies of energy redistribution in isolated polyatomic molecules, a report is made of recent investigations of the internal state distribution in glyoxal (CHOCHO) after this molecule undergoes internal conversion. A molecular beam of glyoxal is pumped from S_0 to a selected vibronic level of S_1 by a pulsed dye laser. Then a second pulsed dye laser, delayed in time sufficiently so that internal conversion takes place, probes the hot band absorption of the pumped molecules by re-excitation into S_1. Information on the internal state distribution is deduced by recording the total (undispersed) fluorescence as a function of probe laser wavelength (excitation spectrum).

The excitation spectrum is broad and featureless in the red but shows sharp structure in the vicinity of the pump laser wavelength. However, the sharp structure depends on the portion of the rotational contour excited. The experimental results show that the redistribution of energy is nonstatistical among the isoenergetic levels. This is explained by assuming that combination bands of low quanta of vibrations are the accepting levels in the internal conversion process and that these accepting levels undergo slow energy redistribution.

Intramolecular energy flow controls the dynamics of unimolecular decomposition when an activated molecule undergoes fragmentation and the redistribution of energy in a radiationless transition when an excited molecule transfers to a different electronic state. Despite intense research efforts, much remains unknown about the behavior of molecules having a high degree of vibrational excitation. A controversy has arisen over the possible mechanisms for energy redistribution.

Two possibilities are that the molecule will display either ergodic or nonergodic behavior.

For vibrational energies near the ground state, the molecular motions will be quasi-periodic; each energy trajectory in phase space is related to the next by using low-order perturbation theory to include effects of anharmonicity. Only a limited portion of phase space is visited in this nonergodic behavior and the energy stays almost completely in the initial combination of excited normal modes. For vibrational energies far above the ground state, the molecular motion becomes quasi-ergodic; for sufficiently large time intervals the energy trajectories are uncorrelated. Almost all regions of the available internal energy phase space are explored uniformly in this ergodic behavior and energy flows rapidly among the modes. The former regime is quantum mechanical (or classical); the latter regime is stochastic and a statistical description is the more appropriate.[1]

These two types of intramolecular energy flow, ergodic and non-ergodic, form the basis for two different descriptions of unimolecular reactions, that of Rice, Ramsperger, Kassel, and Marcus (RRKM) and that of Slater, respectively.[2] The RRKM theory uses a statistical model in which rapid intramolecular energy randomization occurs on a time scale that is short relative to the mean time for the activated molecules to decompose. On the other hand, the Slater theory characterizes the transition state of the activated molecule as having only quadratic terms in its potential energy surface so that internal energy cannot be exchanged between different modes.

The transition between the quasi-periodic and the ergodic regimes is not sharp.[3,4] An outstanding problem is to find the conditions, if any, for which the intramolecular flow of energy is slow compared to other processes, such as photon re-emission, isomerization, fragment-ation, or subsequent chemical reaction. If such conditions could be met, then it may be possible to achieve a "selective chemistry" far different from "thermal chemistry"--a goal long sought by those who hope to control chemical reactions by laser excitation of the reagents. However, based on the numerous successes of the RRKM theory to account for the unimolecular decomposition rates of energized molecules,[2] the belief has grown among many that vibrational energy is rapidly random-ized relative to all other processes at total energies for which the vibrational level density is large. However, the generality of this conclusion, which was based originally on conventional thermal and chemical activation studies, has been contested. A number of recent investigations have raised once again the possibility of nonstatistical behavior.

Trajectory calculations on the methyl isocyanide molecule (CH_3NC) by Bunker and Hase[5] have suggested that this system is an "intrinsic" non-RRKM molecule with an internal bottleneck to the redistribution of energy. This year K. V. Reddy and M. J. Berry[6] reported observing small discrepancies between the calculated and their experimental rate coefficients for CH_3NC isomerization, but much larger deviations for the isomerization of allyl isocyanide. They use laser intracavity absorption to energize the molecules in a state selective manner by excitation into high energy overtones and combination bands. The authors emphasize that the method of preparation of the energy content is critical in observing nonstatistical behavior. They claim that broad distributions over reactant states, as would be expected in thermal and chemical activation studies, would obscure nonergodic effects.

Another example of nonstatistical behavior has been reported by Lee and coworkers[7] in the crossed beam reaction of halogen atoms with substituted olefins. It is inferred from the angular distribution of the products that a long-lived collision complex is formed, having sufficient time to rotate many periods. During this time the complex will execute several thousand vibrations. In chemical activation studies it was found that the average lifetime of the excited halogen addition radical agrees well with the predictions of RRKM theory. However, Lee and coworkers observe that the translational energy distribution of the products is nonstatistical.

We present here a study on the vibrational energy redistribution in isolated glyoxal molecules (CHOCHO) when they undergo internal conversion, a radiationless transition from their first excited electronic state (S_1) to their ground state (S_0). We use the "pump and probe" technique[8] in which a molecular beam of glyoxal is initially pumped from S_0 to a selected vibronic level of S_1, and, after internal conversion occurs, a tunable dye laser is used to probe the hot band absorption of the molecules by re-excitation into S_1. The total fluorescence as a function of probe laser wavelength gives what is called the excitation spectrum.

Glyoxal was chosen for study because its spectroscopy and radiative properties are well known.[9-20] Under collisionless conditions no intersystem crossing ($S_1 \rightarrow T_1$) is detected,[11,12,14] and whatever photochemistry may occur[12,17,18] is likely to be minor and the possible fragments cannot absorb the probe laser wavelength. The lifetimes of the vibrationless level 0^0 and the 8^1 level are 2.4 and 0.87 μsec, respectively,[14] compared to the calculated radiative lifetime of

2.6 − 15 μsec.[14,15] Therefore, more than 50 percent of the energy in S_1 is transferred to S_o by internal conversion. In the case of glyoxal we find that although the molecule has about 22,000 cm^{-1} of energy in excess of the ground state, and a vibrational level density of about $10^8/cm^{-1}$ at this energy, the distribution of internal energy, as determined from the excitation spectra, is distinctly nonstatistical among the isoenergetic vibrational levels of S_o.

It should be emphasized that the method of preparing glyoxal in a specific vibronic level of S_1 is as important as its intrinsic non-ergodic properties in observing nonstatistical behavior. In what follows we propose an explanation for our observations in which the internal conversion process in glyoxal (S_1) populates initially combination bands composed of low quanta of different modes and these accepting levels then undergo slow energy redistribution on the micro-second time scale of our experiment.

Figure 1 illustrates the experimental setup, which is a simple modification of the equipment previously used.[21] An effusive beam of glyoxal is pumped by a pulsed laser tuned to a vibronic transition ($S_o \rightarrow S_1$). A second pulsed laser beam directed anti-parallel to the
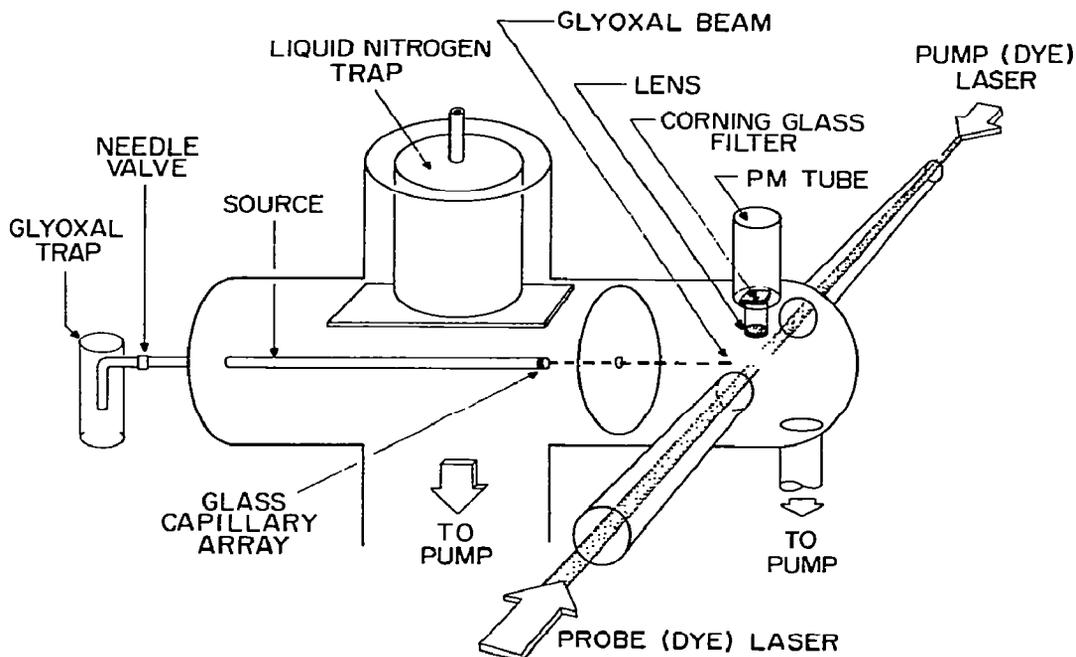

Fig. 1. Laser pump-and-probe setup for studying internal conversion in isolated glyoxal molecules.
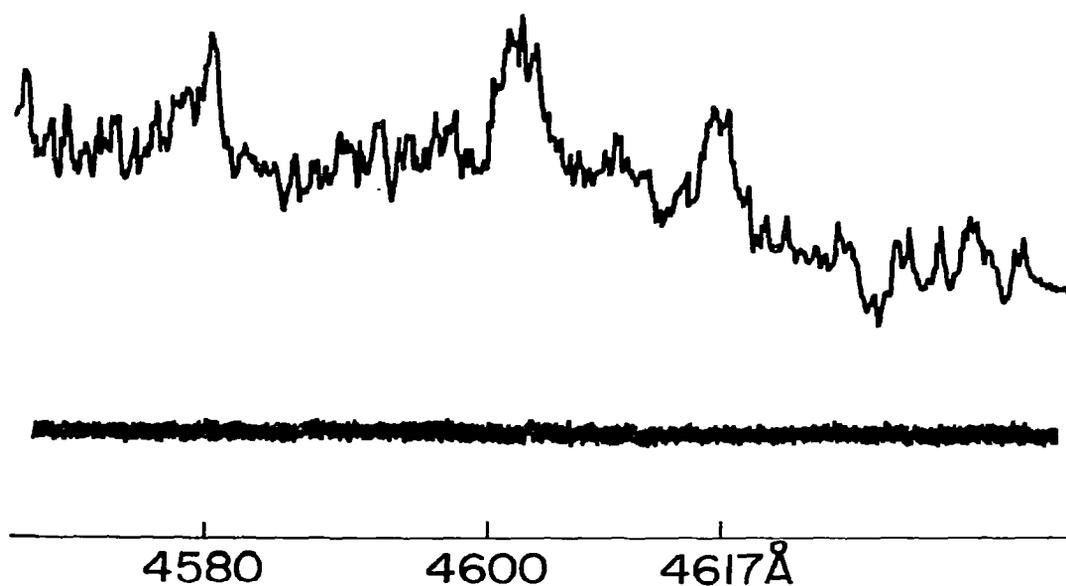
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Fig. 2. Excitation spectrum in the region 4580-4617 Å obtained using the 4403 Å pump laser. The lower trace is obtained when no pump laser is used.
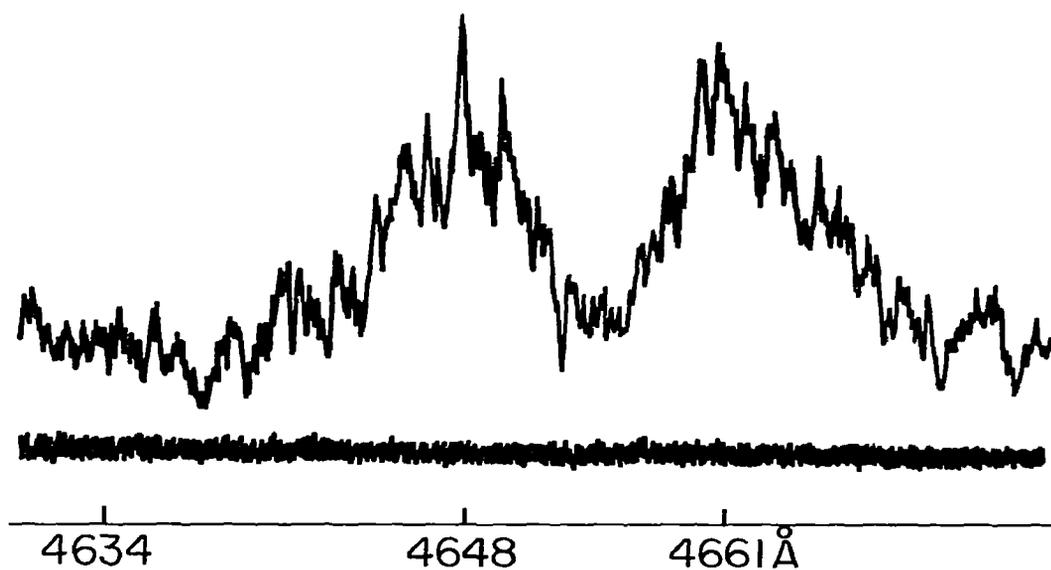

Fig. 3. Excitation spectrum in the region 4634-4661 Å obtained using the 4403 Å pump laser. The lower trace is obtained when no pump laser is used.

first is swept in frequency. By observing the total undispersed fluor-
escence induced by the probe beam as a function of its wavelength,
the energy is studied. The delay time between two lasers is typically
set between 0.7 - 1.2 sec. The emission following probe laser
excitation has a significantly shorter lifetime (in the nanosecond
regime) than the fluorescence from glyoxal induced by the pump laser.
By using filters we determined that the emission spectra has crudely
the same wavelength dependence as the fluorescence from S_1 excited by
the pump laser. We conclude that the emission corresponds to transi-
tions from high vibrational levels of S_1 to S_0.

Figures 2 and 3 show typical excitation spectra. Note the sharp
features observed to the red of the pump frequency (λ pump = 4403 Å;
0.5 Å bandwidth) which can be associated with glyoxal hot band absorp-
tion. Further to the red the excitation spectrum becomes broad and
unresolvable. All these features disappear if the pump laser pulse
does not precede the probe laser pulse.

Studies were also made using a narrow band (0.2 cm^{-1}) dye laser as
the pump source. We found a strong dependence of the sharp features
on the laser wavelength as it is tuned over the rotational contour of
the 8_0^1 band[22] (Fig. 4). The sharp structure can be made to disappear
(Fig. 4b), although no significant effect was observed either in the
far red portion of the excitation spectrum or in the total fluorescence
intensity induced by the pump laser. Over the range that we are able
to delay the probe laser (0.7 to 5 μsec) with respect to the pump
laser, no change in the form of the excitation spectrum is observed.

The present understanding of internal conversion is still in flux
and is a subject of much research activity. However, a starting point
for treating internal conversion in large molecules is provided by the
Fermi golden rule for the rate[23]

$$k_{IC} = \frac{2\pi}{\hbar} \left| V_{mv',nv''} \right|^2 \rho_n \tag{1}$$

where ρ_n is the density of the vibrational levels in the ground state
n and the matrix element, $V_{mv',nv''}$, connecting the excited state mv'
to the ground state nv'' has the approximate form

$$V_{mv',nv''} \propto \sum_k \langle \Psi_m | \frac{\partial U(Q)}{\partial Q_k} | \Psi_n \rangle \langle \chi_{mv_k'} | \frac{\partial}{\partial Q_k} | \chi_{nv_k''} \rangle \prod_{i \neq k} \langle \chi_{mv_i'} | \chi_{nv_i''} \rangle \tag{2}$$

where the total wavefunction is written as the product of an electronic
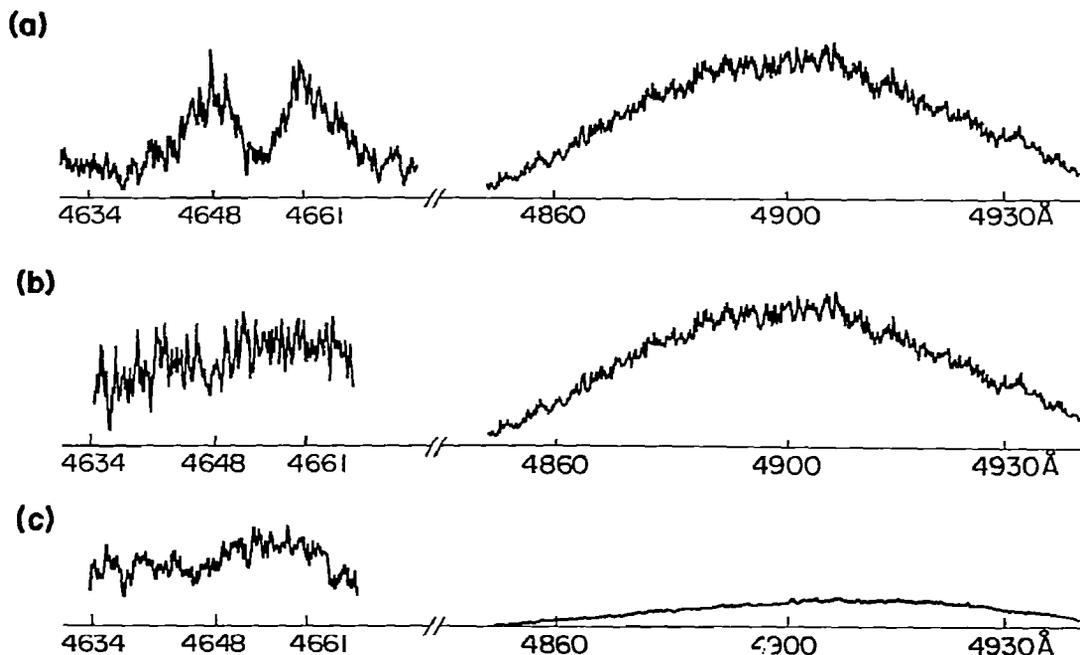wavefunction $\Psi(q,Q)$ and a vibrational wavefunction $\chi(Q)$, and the sum-

(a)

(b)

(c)

Fig. 4. Excitation spectra obtained using (a) broadband (1.5 cm^{-1}) pump laser at 4403 Å; (b) narrow band (0.2 cm^{-1}) pump laser tuned to one part of the rotational contour of the 8_0^1 transition (4403 Å); and (c) no pump laser.

mation is over all normal modes. As can be seen from Eq. (2), the vibronic energy in S_1 is not partitioned equiprobably among all iso-energetic levels in the ground state. Since the symmetry of S_1 is A_u and that of S_0 is A_g, only normal modes of a_u symmetry (called the promoting modes) contribute to the summation in Eq. (2). As Table I shows, there are two such modes, ν_6 and ν_7, of which the latter is believed to contribute more strongly. This is caused by the large change in frequency between S_1 and S_0 for ν_7 compared to ν_6.[14] Finally, the Franck-Condon principle [see the last term in Eq. (2)] favors the energy being deposited in ground state levels having a large vibrational overlap with the excited level. Thus the internal conversion process initially selects only a small subset of the manifold of iso-energetic ground state levels.

After a time on the order of a microsecond, a probe laser interrogates the molecule. If the initial distribution of vibrational energy levels in S_0 does not undergo extensive energy redistribution, then structured features will appear in the excitation spectrum in the

vicinity of the pump laser wavelength. Most of the modes have a lower vibrational frequency in S_1 than in S_0 (see Table I). Therefore many of the combination bands will absorb energy which is red shifted relative to the pump laser wavelength. Indeed, only a limited number of combination bands can absorb energy in the wavelength region near the pump laser and these combination bands must contain overtones of ν_7 and/or ν_{12} to offset the red shift of the other modes. Consequently, one expects to observe sharper structure in the blue than the red.

Let us consider in more detail the red shift in the excitation spectrum. In addition to the fact that the vibrational frequencies are lower on the average in S_1 than in S_0, there is another contribution to the red shift. As the vibrational quantum number $v_k"$ of mode k increases, transitions to $v_k' \neq v_k"$ become stronger. Thus the population of high overtones of a mode will cause more extensive red shifting than the population of combination bands having the same energy. In this experiment no strong signal could be observed when the probe laser is scanned over the wavelength region 5000-7000 Å. Because the excitation spectrum shows relatively small red shifting, we conclude that combination bands of low overtones are primarily responsible for accepting the energy, i.e. are the accepting levels. In many theoretical treatments of radiationless processes, high overtones are assumed to accept the energy. This study on glyoxal suggests a counterexample.

The change of the structured portion of the excitation spectrum with pump laser bandwidth points to a rotational dependence of the radiationless process. This may be caused by (a) different vibrational levels of S_0 coming into resonance with the rovibronic level of S_1 at different excitation energies and (b) a rotational dependence of the internal conversion rate. The latter cannot be seen in Eq. (2) which was derived by assuming that the projection of the rotational angular momentum on the molecular top axis is constant. Rotational dependence of radiationless transitions has been observed previously in several other molecules.[24-26]

Based on the RRKM theory the vibrational energy redistribution rate is expected to be proportional to the density of vibrational levels. At the pump energy in this experiment (~ 22,000 cm^{-1}), the vibrational level density is so high (about 10^8/cm^{-1}) that it might be supposed that the internal energy is statistically distributed among all iso-energetic levels even though the internal conversion process selectively deposits energy in a few levels. Moreover, the energy redistribution should occur rapidly, i.e. on the order of picoseconds, giving a width to each accepting level.

To test this picture a computer program was written that determined the spectral transition for each isoenergetic level in the range of the excitation spectrum where signal was observed. Some simple approximations were made. Each level was assumed to have a width of 1 cm^{-1}. Only $\Delta v=0$ transitions were allowed. Figure 5 presents the computer simulated excitation spectrum.

A comparison of Fig. 5 with Figs. 2 and 3 shows that this model is unable to reproduce our observations. This conclusion still holds if $\Delta v = \pm 1$ transitions are also included. We take this as a demonstration that part of the energy following internal conversion is <u>not</u> statistically distributed among all isoenergetic levels, even after several microseconds have elapsed. Not only is the presence of sharply structured features evidence for nonstatistical energy redistribution but the fact that these features depend sensitively on the pump wavelength also supports this conclusion. This study may be the first instance where quasi-periodic levels at high vibrational energies have been experimentally detected. It may be possible in the future to assign these structured features. The computer program we have written already is able to predict the locations of such features within a few reciprocal centimeters of where they are found. If this possibility is
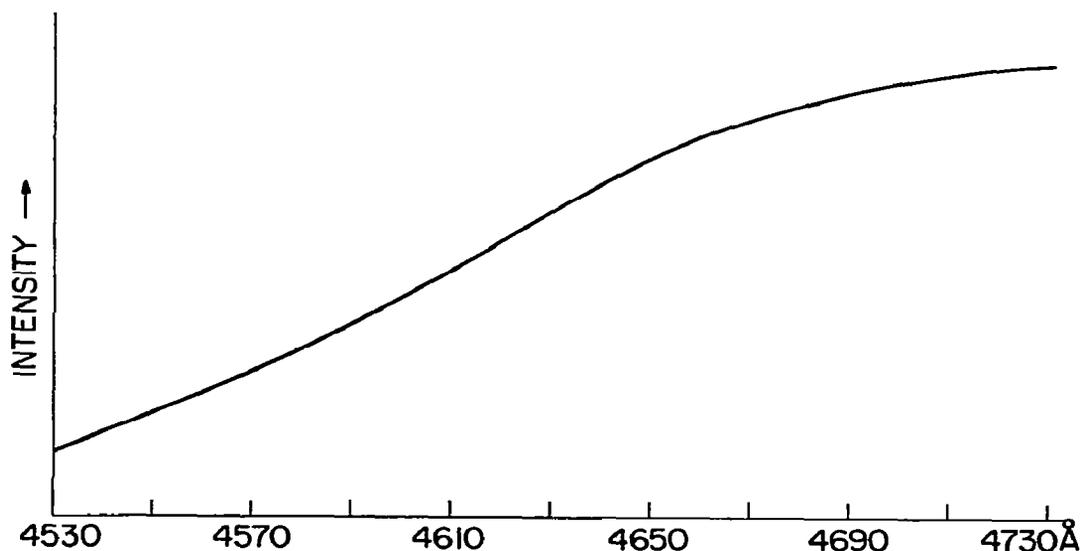

Fig. 5. Simultated excitation spectrum for glyoxal assuming the energy of internal conversion is partitioned statistically among the isoenergetic levels. When the density of transitions exceeded 15 per reciprocal centimeter, the spectrum was taken as structureless within this region.

TABLE 1
Vibrational Frequencies in Glyoxal[16]

Symmetry	Vibration	^1A_g	^1A_u
a_g	ν_1 C-H stretching	2844	2809
	ν_2 C=O stretching	1745	1391
	ν_3 C-H rocking	1338	
	ν_4 C-C stretching	1065	955
	ν_5 C-C=O bending	550	509
a_u	ν_6 C-H wagging	801	719
	ν_7 torsional	127	233
b_g	ν_8 C-H wagging	1048	735
b_u	ν_9 C-H stretching	2835	
	ν_{10} C=O stretching	1732	
	ν_{11} C-H rocking	1312	
	ν_{12} C-C-O bending	338	380

realized, then the high vibrational levels of ground state molecules
are opened for spectroscopic study.

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