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IR ABSORPTION SPECTRUM OF CrO_2Cl_2 MOLECULES FOR HIGH-LYING STATES OF THE VIBRATIONAL QUASI-CONTINUUM

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A new approach to the spectroscopy of highly excited vibrational states of polyatomic molecules has been elaborated. The molecules of CrO_2Cl_2 were prepared in states with a vibrational energy of the ground electronic term A_1 of $\approx 19000\text{ cm}^{-1}$ by means of internal conversion of electronic energy from the electronic state B_1 excited by laser radiation. The spectroscopy of the vibrationally excited molecules has been carried out in the region of the ν_6 and ν_1 bands with diode and CO_2 lasers. The fwhm of the obtained spectrum was $\approx 15\text{ cm}^{-1}$. The intermode interaction in CrO_2Cl_2 has been theoretically analyzed, and the calculated spectrum compared with that measured experimentally. The time evolution of the spectrum of vibrationally excited CrO_2Cl_2 molecules has been studied. The average energy transferred per one collision with unexcited CrO_2Cl_2 molecules was equal to $\langle \Delta E \rangle \approx 1200\text{ cm}^{-1}$.

1. Introduction

Much importance has recently been attached to processes connected with strong vibrational excitation of polyatomic molecules [1]. The spectroscopy of vibrationally excited molecules yields valuable information for understanding these processes. A characteristic feature of spectra of vibrationally excited molecules is homogeneous broadening of separate spectral lines, which results from the mixing of closely spaced vibrational states due to intermode anharmonic coupling. Such mixing leads to the formation of the vibrational quasi-continuum (QC) of the molecule. To date, there have been just a few experiments that directly probe the QC. It is often difficult to theoretically interpret such experiments because of the inhomogeneous broadening caused by the distribution of molecules over vibrational states. Such broadening can be observed, for instance, when using the standard method of preparation of molecules in QC-states – in the IR multiple-photon excitation [1]. In order to study a homogeneous spectrum in the QC one should get rid of the spectral broadening related to the distribution of

molecules over vibrational states. For spectroscopy of high-lying vibrational states, methods which allow to probe the monoenergetic states of the QC such as direct spectroscopy of high overtones and preparation of molecules in high-lying vibrational states through non-radiative transitions in the process of internal conversion are preferable.

Some works on the spectroscopy of high overtones of polyatomic molecules [2–5] have been published at present. For the acetylene molecule, narrow vibrational–rotational lines with Doppler width have been observed for the fifth and sixth overtones of the C–H stretch mode, i.e. for vibrational energies from 14900 to 18500 cm^{-1} [2]. In SiHCl_3 and SiH_2Cl_2 molecules the width of the vibrational–rotational contour does not grow with the change of the overtone number from $\Delta v = 6$ to $\Delta v = 9$ for the Si–H vibration, vibrational energies varying from 12000 to 18000 cm^{-1} [3]. For more complex molecules the situation changes. In the case of benzene widths from 50 to 100 cm^{-1} are observed depending on the number of the C–H overtone [4]. For the more complex molecule tetramethyldioxetane, the width of the fifth over-

tone of the C–H mode is close to 100 cm^{-1} [5].

The purpose of the present paper is to study the IR absorption spectrum of CrO_2Cl_2 molecules prepared quasi-monoenergetically in states with a vibrational energy of $\approx 19000\text{ cm}^{-1}$, which is, just 4000 cm^{-1} below its dissociation limit. The preparation of molecules in high-lying vibrational states was performed in the process of internal conversion of electronic to vibrational energy when the molecules absorb visible laser radiation. As a result, a comparatively narrow IR absorption band, corresponding to transitions from states with an energy of $\approx 19000\text{ cm}^{-1}$, was observed. The time evolution of the spectrum obtained is studied and the data of the experiment are compared to theoretical results.

2. Spectral characteristics of the CrO_2Cl_2 molecule

The lower electronic states of CrO_2Cl_2 are well studied [6,7]. The available experimental results are reviewed in ref. [7]. Below the dissociation limit of the ground electronic state 1A_1 (fig. 1) there exist two singlet states A_2 and B_1 with 0–0 transition energies of 16970 and 17248 cm^{-1} , respectively. The transitions to the A_2 state are symmetry forbidden. The vibrational level density

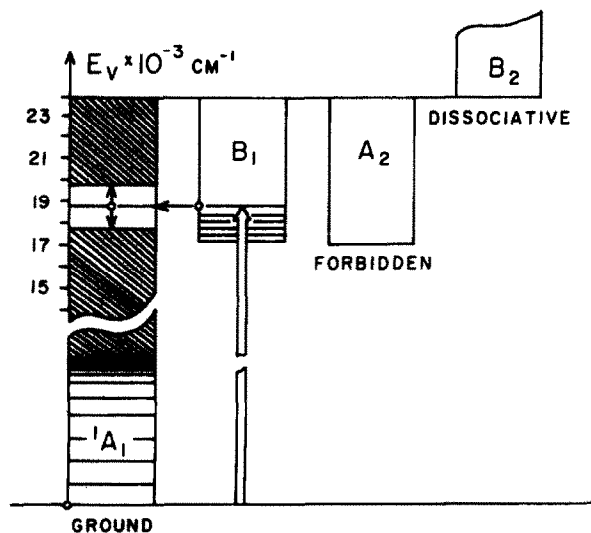


Fig. 1. Scheme of the lower electronic–vibrational states of the CrO_2Cl_2 molecule.

of the ground electronic state in the region of 17248 cm^{-1} is equal to 6.5×10^6 levels per cm^{-1} . Because of non-adiabatic coupling of the ground A_1 and the excited B_1 electronic state the vibrational levels of B_1 decay non-radiatively. Experimentally, such transitions display themselves in a decrease of the fluorescence decay time with the increase of the exciting radiation frequency [6]. Fluorescence is not observed altogether when the states with an energy exceeding the 0–0 transition by more than 450 cm^{-1} are excited. In our experiment the second harmonic of a Nd:YAG laser was used to excite CrO_2Cl_2 molecules, its frequency exceeding the energy of the 0–0 transition by 1550 cm^{-1} . The absorption cross section at the excitation wavelength ($\lambda = 532\text{ nm}$) was equal to $3.8 \times 10^{-19}\text{ cm}^2$. As a result of non-radiative transitions, the molecules in such energy levels ended up in the isoenergetic vibrational state of the ground electronic term. The quasi-monoenergetic ensemble of molecules prepared in this way was then probed with IR radiation.

Vibrational frequencies and rotational constants of the CrO_2Cl_2 molecule [7,8] are tabulated (see tables 1 and 2). The characteristic feature of this molecule is the presence of a larger number of low-frequency vibrations. There are just two high-frequency modes ν_1 and ν_6 which are active in the IR absorption spectrum. The IR multiphoton excitation of CrO_2Cl_2 has been investigated in a number of works [12–15].

In our experiment the CrO_2Cl_2 molecules were

Table 1
Frequencies of the normal vibrations of CrO_2Cl_2 ^{a)}

C_{2v} symmetry	Mode	Frequency (cm^{-1})	Vibrations
$A_1(z)$	ν_1	995 ^{b)}	Cr–O stretch
	ν_2	475 ^{b)}	Cr–Cl stretch
	ν_3	356 ^{b)}	CrO_2 bend
	ν_4	140 ^{c)}	CrCl_2 bend
A_2	ν_5	224 ^{c)}	$\text{O}_2\text{–Cl}_2$ torsion
$B_1(x)$	ν_6	1002 ^{b)}	Cr–O stretch
	ν_7	215 ^{c)}	CrO_2 rock
$B_2(y)$	ν_8	500 ^{b)}	Cr–Cl stretch
	ν_9	257 ^{c)}	CrCl_2 rock

^{a)} The results are taken from ref. [7].

^{b)} Obtained in gas [9].

^{c)} Obtained in liquid [10,11].

Table 2
Rotational constants ^{a)} of CrO_2Cl_2 (cm^{-1})

A	0.1073
B	0.0620
C	0.0521

^{a)} From ref. [7].

probed with IR radiation in the region of the ν_1 and ν_6 bands.

3. Experimental

The absorption spectrum of vibrationally excited CrO_2Cl_2 was investigated using the arrangement schematically presented in fig. 2. The molecules were excited by the second harmonic of a Nd:YAG laser with $\lambda = 532$ nm. Its maximum energy was 20 mJ. The pulse duration was equal to 15 ns. The spectral bandwidth was 0.2 cm^{-1} . The diameter of the exciting radiation beam in the cell was 8 mm.

The induced absorption spectrum of the excited

molecules was probed by IR lasers. Three types of IR lasers were used to cover the widest possible range of induced absorption – the diode PbSnSe laser was operated within the range $950\text{--}1020 \text{ cm}^{-1}$, and the $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ lasers in the range $890\text{--}990 \text{ cm}^{-1}$. The probe-radiation power was not more than several milliwatt for the CO_2 laser, and several hundred microwatt for the diode laser. The Nd:YAG and the diode lasers were synchronized with an accuracy of 30 ns.

The exciting and the probe beams were directed to a glass cell, 50 cm long, with NaCl windows. After the cell, the IR radiation was focused onto the slit of the monochromator. The monochromator was used for frequency control of the probe radiation and acted as a filter cutting off scattered radiation.

After the monochromator, the IR radiation was recorded with an IR detector designed on the basis of Si:B crystals. The detector worked at liquid-helium temperature; its sensitivity threshold being equal to $10^{-11} \text{ W/Hz}^{1/2}$, and the dynamic range 10^7 . The time resolution was 150 ns. The recording system allowed us to detect variations of

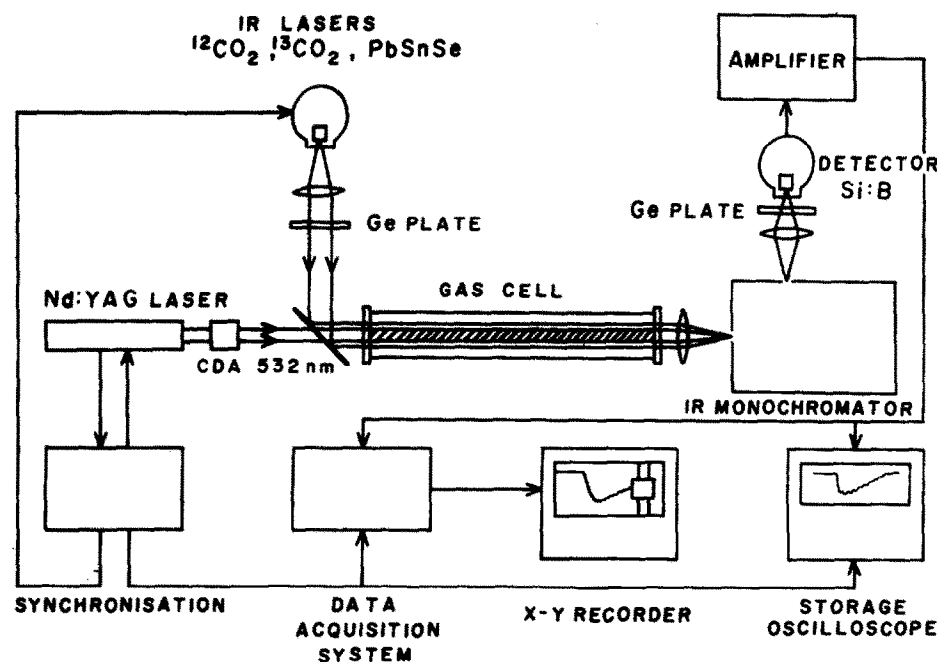


Fig. 2. Scheme of the experimental arrangement.

0.1% in the absorption with the signal-to-noise ratio being equal to 3.

We measured the IR absorption (bleaching) induced by the second-harmonic radiation of the Nd:YAG laser. This absorption (bleaching) is characterized by the coefficient of induced absorption (bleaching) $K_{\text{ind}}(t)$. The change of the probe-radiation intensity is expressed as

$$\Delta I(t) = I_0 \exp(-KL) [1 - \exp(-K_{\text{ind}}(t)L)], \quad (1)$$

where I_0 is the incident radiation intensity, K the coefficient of linear absorption, and L the cell length. With $K_{\text{ind}}L \ll 1$,

$$K_{\text{ind}}(t) \approx \Delta I(t)/LI_0 \exp(-KL) = \Delta I(t)/IL, \quad (2)$$

where I is the intensity of probe radiation after passing the cell in the absence of pumping light.

4. Experimental results

Fig. 3 shows oscillograms of induced absorption (bleaching) pulses taken with probing at (a) 931.0, (b) 966.2 and (c) 989.6 cm^{-1} . The spectrum of IR absorption of CrO_2Cl_2 is consistent with the ν_1 and ν_6 modes. The pressure of CrO_2Cl_2 gas in the cell was 0.5 Torr.

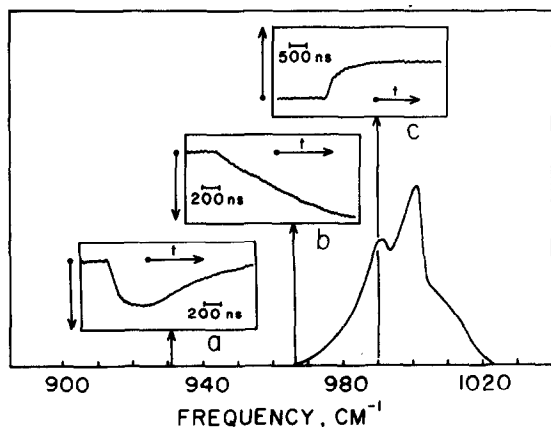


Fig. 3. Oscillograms of induced absorption (bleaching) pulses taken with probing at (a) 931.0, (b) 966.2 and (c) 989.6 cm^{-1} . The spectrum of IR absorption of CrO_2Cl_2 is consistent with the ν_1 and ν_6 modes. The pressure of CrO_2Cl_2 gas in the cell was 0.5 Torr.

molecule was probed at the frequency of 930 cm^{-1} , an induced absorption signal with a short risetime was observed. The risetime of induced absorption remained constant as the pressure of CrO_2Cl_2 gas in the cell ranged from 0.05 to 0.5 Torr. The maximal amplitude of that signal changed linearly with the gas pressure in the cell (fig. 4). Thus, the induced absorption at 930 cm^{-1} was collisionless and related to monomolecular processes resulting from the excitation of the CrO_2Cl_2 molecule. The pulse amplitude of induced absorption at 930 cm^{-1} changed linearly both with the exciting radiation fluence in the range from 0 to 20 mJ/cm^2 (fig. 5) and the probe-radiation power within 0–5 mW (fig. 6).

As the probing frequency approached the absorption bands ν_1 and ν_6 of unexcited molecules, the induced absorption pulse shape changed significantly. The risetime of the pulse became longer, which points to the presence of collision-induced absorption in this frequency range. When probing was performed in the ν_1 and ν_6 bands a bleaching signal was observed, which corresponds to the depletion of some lower vibrational-rotational levels of CrO_2Cl_2 . The risetime of the bleaching pulse was defined by the time constant of the recording system.

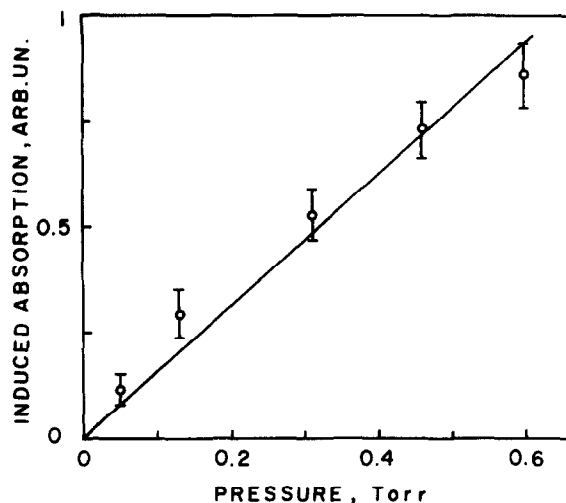


Fig. 4. Dependence of the induced absorption amplitude on the pressure of CrO_2Cl_2 gas obtained with probing at 930 cm^{-1} . The exciting radiation fluence was 20 mJ/cm^2 .

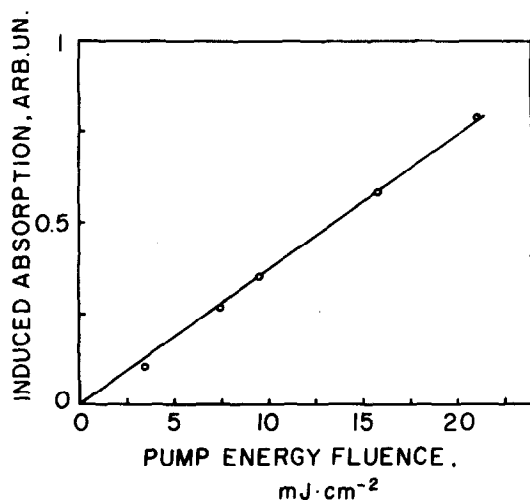


Fig. 5. Dependence of the induced absorption amplitude on the exciting radiation fluence obtained with probing at 930 cm^{-1} . The pressure of CrO_2Cl_2 gas in the cell was 0.5 Torr.

Fig. 7 shows induced absorption spectra observed at different delay times after the exciting pulse of the second harmonic of the Nd:YAG laser. These spectra were obtained at time delays of 0.1, 0.25, 0.5 and 1 μs . The induced absorption spectrum produced 0.1 μs after the exciting pulse

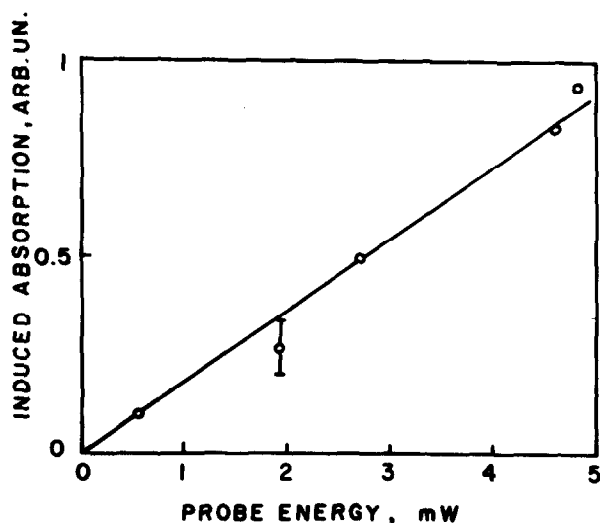


Fig. 6. Dependence of the induced absorption amplitude on the probing radiation power at 930 cm^{-1} . The pressure of CrO_2Cl_2 gas in the cell was 0.5 Torr. The exciting radiation fluence was $20 \text{ mJ}/\text{cm}^2$.

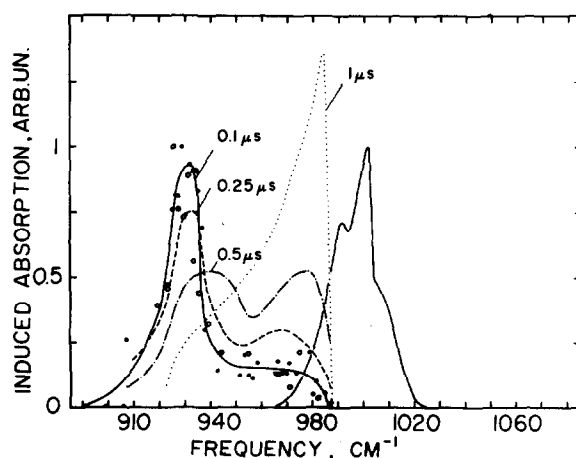


Fig. 7. Induced absorption spectra taken at 0.1, 0.25, 0.5 and 1.0 μs after the exciting pulse. The circles stand for the induced absorption spectrum (solid curve) at 0.1 μs . Filled and open circles denote the probing by $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$ lasers, respectively. The exciting radiation fluence was $20 \text{ mJ}/\text{cm}^2$. The gas pressure in the cell was 0.5 Torr. The linear IR absorption spectrum of CrO_2Cl_2 corresponding to the ν_1 and ν_6 modes (to the right-hand side) is given for comparison. The amplitude of this spectrum is given without relation to the induced absorption spectrum amplitude.

was rather narrow, its width being 15 cm^{-1} (fwhm). At the blue side of this band there was a comparatively low-intensity wide pedestal. At a frequency of $\approx 980 \text{ cm}^{-1}$ the amplitude of this pedestal was reduced because of the induced bleaching of the fundamental absorption band. As the time delay increased the induced absorption band intensity $K(\omega, t)$ dropped, the band broadened, its maximum shifted towards the fundamental bands ν_1 and ν_2 . Simultaneously, the collisional absorption occurred at the red wing of the ν_1 and ν_6 bands. It should be noticed that the induced absorption band $K(\omega, t = 0.1 \mu\text{s})$ was somewhat narrower than the inhomogeneously broadened absorption bands ν_1 and ν_6 of the CrO_2Cl_2 molecule with $T = 300 \text{ K}$. Due to the presence of a large number of low-frequency vibrations (see table 1) at room temperature only a quarter of the CrO_2Cl_2 molecules were in the ground state. It is known that when narrow-band laser radiation is used for excitation, one can observe a rotational structure in the electronic-vibrational spectrum of the $B_1 \leftarrow {}^1A_1$ band [7]. So,

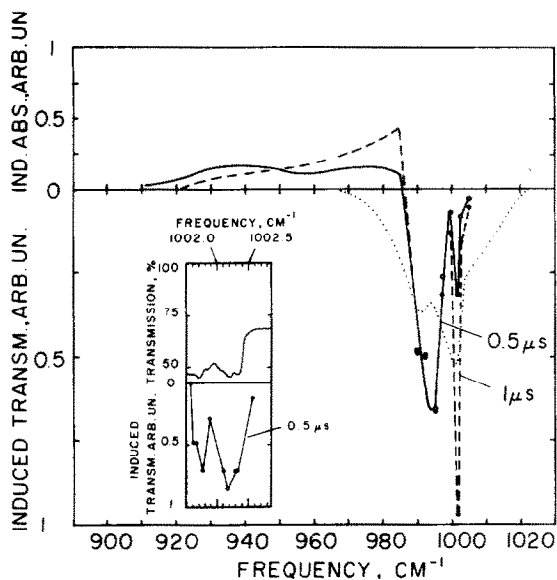


Fig. 8. Dependence of induced bleaching on the probing radiation frequency of the semiconductor laser. The solid and dashed lines correspond to the probing 0.5 and 1.0 μs after the exciting pulse. The exciting radiation fluence was 20 mJ/cm^2 . The gas pressure in the cell was 0.5 Torr. The dotted line shows, for comparison, the IR absorption spectrum of the ν_1 and ν_6 bands of CrO_2Cl_2 . The inserted part of the induced bleaching spectrum corresponds to the peak at 1002 cm^{-1} . The corresponding part of the IR absorption spectrum was taken with a semiconductor laser.

in the case of narrow-band laser radiation the inhomogeneous broadening of the induced absorption band $K(\omega, t=0)$ may appear to be smaller than the broadening inherent to the fundamental bands ν_1 and ν_6 since not all of the molecules distributed over low vibrational-rotational levels at $T = 300$ K will absorb the exciting radiation. Fig. 8 shows the induced bleaching band obtained at the time delays of 0.5 and 1 μs after the exciting pulse when probing was done with the diode laser. The width of the bleaching band was equal to 9 cm^{-1} (fwhm). In the region of the steep edge of the Q-branch of the ν_6 band at 1002 cm^{-1} , there occurred a bleaching peak that is collisional by nature. A more detailed structure of this peak is shown in fig. 8 together with the corresponding part of the absorption spectrum of the ν_1 and ν_6 bands.

5. Calculation of the induced absorption spectrum

So far there is no universal approach to the calculation of the spectrum of molecules with a high level of vibrational excitation. The cause of drastic changes in the spectral properties of the molecule in the vibrational quasi-continuum (QC) is not in dispute [16–24]. Due to intermode anharmonicity the close-lying vibrational states are mixed and this makes that the IR active mode transition strength is redistributed. Thus, instead of separate lines of transitions allowed in the harmonic approximation the spectrum is a quasi-continuous broadened band. This band broadening in the QC is called homogeneous.

The main advantage of the experimental method used is the creation of a population distribution characterized by a high average energy and comparatively narrow width. This diminishes the role of inhomogeneous broadening and permits us to determine or to estimate QC parameters.

The method of description of the highly excited molecular spectrum is based mainly on the results of ref. [17] (see also ref. [24]). Additional assumptions are adopted just for the CrO_2Cl_2 molecule and allow us to give concrete expressions for model parameters. These assumptions are listed below. The hypothesis that we use here is that the excitation level of “hot” molecules ($\approx 19 \times 10^3$ cm^{-1}) does belong to the QC region and the molecule undergoes rapid statistical equilibrium prior to probing by weak IR radiation, so the “initial state” of the molecule can be treated as a microcanonical ensemble. Let us formulate simplifying model assumptions the introduction of which is reasoned by poor information on the excitation parameters of CrO_2Cl_2 rather than by difficulties in calculation.

(1) The population of levels of “hot” molecules after excitation is determined only by the Boltzmann distribution over lower states and by different excitation efficiencies (see section 4). At this stage the role of residual inhomogeneous broadening was completely excluded, i.e. in the model calculation the ensemble of “hot” molecules was considered to be strictly monoenergetic. Transitions with changing rotational quantum numbers are not taken into account either.

(2) In the region of probing ($\approx 1000 \text{ cm}^{-1}$) two modes are IR active, ν_1 and ν_6 . The strong similarity between the symmetry of the CrO_2Cl_2 molecule (C_{2v}) and a tetrahedron (T_d) enables one to suggest that the vibration $\nu_6(B_1)$ is characterized by a larger oscillator strength. (For the tetrahedron the fully symmetrical vibration $\nu_1(A_1)$ is not active in the IR spectrum.) Therefore, to simplify the model, the ν_6 band will be referred hereafter as the only IR active vibration in the frequency range under study. The validity of our assumption can be proved by standard methods of high-resolution spectroscopy.

Let us turn to the inference resulting from the general theory of non-linear dynamical systems with many degrees of freedom [25] and some QC investigations [16,20,24], i.e. the relevance of intermode resonances which define the QC properties in every specific case. This inference is based on the fact that the harmonic states that are close in energy (a small defect of intermode resonance) and interact on account of low-order anharmonicity can be mixed effectively.

Among the symmetry-allowed third-order resonances of CrO_2Cl_2 with defects of less than 100 cm^{-1} , two include the ν_1 mode: $2\nu_8 - \nu_1 \approx 5 \text{ cm}^{-1}$ (anharmonic interaction $\hat{V} \propto \hat{x}_8^2 \hat{x}_1$) and $\nu_1 - 2\nu_2 \approx 45 \text{ cm}^{-1}$ ($\hat{V} \propto \hat{x}_2^2 \hat{x}_1$). There are no such third-order resonances which include the ν_6 mode. Fourth-order resonances are also more favourable for the ν_1 mode as compared to ν_6 . So the following scheme of mode interaction is proposed for these molecules: ν_6 is coupled with ν_1 by the fourth-order anharmonic term

$$\hat{V} = V_{1,6} \hat{x}_1^2 \hat{x}_6^2 \quad (3)$$

($V_{1,6}$ is the anharmonic coupling constant) with the defect Δ :

$$\Delta = 2\nu_6 - 2\nu_1 \approx 14 \text{ cm}^{-1} \quad (4)$$

and the interaction of ν_1 with other modes is strong enough to ensure the assumed mixing of this mode with other ones. We use a normalization of interaction (3) such that

$$\begin{aligned} \langle \nu_1 + 2, \nu_6 - 2 | \hat{V} | \nu_1, \nu_6 \rangle \\ = V_{1,6} (v_1 + 1)(v_1 + 2)v_6(v_6 - 1). \end{aligned} \quad (5)$$

The remainder of the calculation is based on separating the IR active mode (in our case ν_6) from all the vibrations of the molecule and the consideration that all other modes are a bath [17–21,24]. Let us designate the levels of the subcontinuum without the ν_6 mode, i.e. the bath states, as $|\epsilon\rangle$. Without interaction (3) there is quasi-degeneracy expressed as

$$|v_6 = 0, \epsilon = E\rangle, \dots |v_6 = m, \epsilon = E - m\nu_6\rangle, \dots \quad (6)$$

The occupation number v_6 in this case remains a good quantum number, and the bath states are mixed harmonic ones. Any changes in the structure of the bath levels when anharmonic coupling (3) is not taken into account do not affect the absorption spectrum since, according to our assumptions, the oscillator strength is determined only by the ν_6 mode. So, when $V_{1,6} = 0$ the transition matrix elements are

$$|\langle v_6 = m; \epsilon | \hat{\mu}(\hat{x}_6) | v_6 = m + 1; \epsilon' \rangle|^2 \propto \delta(\epsilon - \epsilon'). \quad (7)$$

In (7) $\hat{\mu}$ is the dipole moment operator.

To calculate the spectrum a stronger assumption than the existence of the QC in the energy region of probed “hot” levels is used, i.e. that the markovian approximation is valid for the intramolecular relaxation. In particular, this means that the initial evolution of the population p_v created in the $|v, \epsilon\rangle$ state is described by the simple exponential decay:

$$dp_v/dt = -\Gamma_v p_v. \quad (8)$$

Under this approximation the Bloch equations are obtained in ref. [17] for the reduced density matrix $\rho(N; v, v')$ where the index N corresponds to the states of the bath, and v, v' are occupation numbers of the IR active mode (our designations are not the same as in ref. [17]; see also ref. [24]). The whole energy of the molecule is marked by the index $k = N + v$. Induced absorption (emission) of the photon from the quasi-resonant field is described by the transitions $N \rightarrow N, v \rightarrow v + 1, k \rightarrow k + 1$ ($N \rightarrow N, v \rightarrow v - 1, k \rightarrow k - 1$). Let Ω_0 be the interaction of the ν_6 mode with the field,

$$\Omega_0 = \mu_{01} \mathcal{E} / 2\hbar, \quad (9)$$

where \mathcal{E} is the amplitude of the field, μ_{01} is the matrix element of the dipole moment for the transition $v=0 \rightarrow v=1$. Then the absorption spectrum of the system excited to energy level k is defined as

$$I = - \lim_{\Omega_0 \rightarrow 0} \frac{d}{dt} \sum_{N+v=k} \frac{\rho(N; v, v)}{\Omega_0^2}. \quad (10)$$

For convenience the spectra of up and down transitions can be considered separately. The condition $\Omega_0 \rightarrow 0$ allows us to restrict the whole Bloch equations system to the one for the levels pictured in fig. 9a. As the energy level k is fixed we can use simpler designations:

$$\begin{aligned} p_v &= \rho(N; v, v), \\ \tilde{p}_v &= \rho(N+1; v, v), \\ \alpha_v &= \rho(N; v, v+1) - \rho(N; v+1, v), \\ \beta_v &= \rho(N; v, v+1) + \rho(N; v+1, v). \end{aligned} \quad (11)$$

So p_v and \tilde{p}_v are the populations of the energy levels k and $k+1$ with fixed value v , respectively. α_v and β_v are antisymmetrical and symmetrical combinations of non-diagonal density matrix elements.

The Bloch equations from which it is possible to obtain p_v values and consequently the spec-

trum (10) have the form [17]:

$$\begin{aligned} dp_v/dt &= -(\Gamma_{v,v-2} + \Gamma_{v,v+2})p_v \\ &\quad + \Gamma_{v-2,v}p_{v-2} + \Gamma_{v+2,v}p_{v+2} - i\Omega_v\alpha_v, \end{aligned} \quad (12a)$$

$$\begin{aligned} d\tilde{p}_v/dt &= -(\tilde{\Gamma}_{v,v-2} + \tilde{\Gamma}_{v,v+2})\tilde{p}_v \\ &\quad + \tilde{\Gamma}_{v-2,v}\tilde{p}_{v-2} + \tilde{\Gamma}_{v+2,v}\tilde{p}_{v+2} + i\Omega_{v-1}\alpha_{v-1}, \end{aligned} \quad (12b)$$

$$\begin{aligned} d\alpha_v/dt &= -i\delta_v\beta_v + 2i\Omega_v(\tilde{p}_{v+1} - p_v) \\ &\quad - \frac{1}{2}[\Gamma_{v,v-2} + \Gamma_{v,v+2} \\ &\quad + \tilde{\Gamma}_{v+1,v-1} + \tilde{\Gamma}_{v+1,v+3}]\alpha_v \\ &\quad + (\Gamma_{v-2,v}\tilde{\Gamma}_{v-1,v+1})^{1/2}\alpha_{v-2} \\ &\quad + (\Gamma_{v+2,v}\tilde{\Gamma}_{v+3,v+1})^{1/2}\alpha_{v+2}, \end{aligned} \quad (12c)$$

$$\begin{aligned} d\beta_v/dt &= -i\delta_v\alpha_v - \frac{1}{2}[\Gamma_{v,v-2} + \Gamma_{v,v+2} \\ &\quad + \tilde{\Gamma}_{v+1,v-1} + \tilde{\Gamma}_{v+1,v+3}]\beta_v \\ &\quad + (\Gamma_{v-2,v}\tilde{\Gamma}_{v-1,v+1})^{1/2}\beta_{v-2} \\ &\quad + (\Gamma_{v+2,v}\tilde{\Gamma}_{v+3,v+1})^{1/2}\beta_{v+2}. \end{aligned} \quad (12d)$$

The introduced designation have the following meaning: δ_v is the detuning from resonance for the transition $v \rightarrow v+1$ ($\delta_v = \nu_{\text{laser}} - \bar{\nu}_v$). Both intra- and scalar inter-mode anharmonicities define this value. Γ and $\tilde{\Gamma}$ are the rates of intramolecular relaxation for the energy level k and $k+1$. For the overall rate Γ_v it follows from (8) that

$$\Gamma_v = \Gamma_{v,v-2} + \Gamma_{v,v+2}. \quad (13)$$

The v -dependence of the field interaction values Ω_v is that of the harmonic oscillator:

$$\Omega_v = \Omega_0(v+1)^{1/2}. \quad (14)$$

It was accounted for that interaction (3) couples only the levels with the same parity of quantum number v . To minimize the number of calculational parameters, the proper dephasing broadening was neglected.

The rates Γ and $\tilde{\Gamma}$ are connected by the relations:

$$\begin{aligned} \Gamma_{v,v+2}/\Gamma_{v+2,v} &= D_{v+2}/D_v, \\ \tilde{\Gamma}_{v,v+2}/\tilde{\Gamma}_{v+2,v} &= D_{v+1}/D_{v-1}. \end{aligned} \quad (15)$$

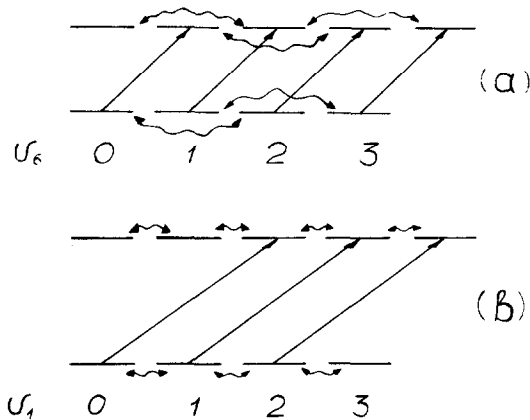


Fig. 9. Level schemes for determination of the spectrum: (a) ν_6 up-transitions in the CrO_2Cl_2 molecule; (b) ν_1 overtone in the "molecule" without ν_6 . Wavy lines denote intramolecular relaxation, straight lines denote weak probing field.

Here D_v is the density of vibrational bath states at $N = k - v$. From (12a) an expression can be derived in order to calculate spectrum (10):

$$\frac{d}{dt} \sum p_v = -i \sum \Omega_v \alpha_v. \quad (16)$$

As the solution of (12) is needed only at $\Omega_0 \rightarrow 0$ it is possible to use a perturbation treatment, when (12) is solved under quasi-stationary conditions

$$\dot{\alpha}_v = \dot{\beta}_v = 0, \quad \dot{p}_v = 0, \quad p_v = D_v / \sum D_v = p_v(\text{st}). \quad (17)$$

So the problem of determination of the spectrum is reduced to solving the linear system of algebraic equations:

$$\begin{aligned} & -i\delta_v \beta_v - \frac{1}{2}(\Gamma_{v,v-2} + \Gamma_{v,v+2} \\ & + \tilde{\Gamma}_{v+1,v-1} + \tilde{\Gamma}_{v+1,v+3})\alpha_v \\ & + (\Gamma_{v-2,v} \tilde{\Gamma}_{v-1,v+1})^{1/2} \alpha_{v-2} \\ & + (\Gamma_{v+2,v} \tilde{\Gamma}_{v+3,v+1})^{1/2} \alpha_{v+2} = 2i\Omega_v p_v(\text{st}), \\ & -i\delta_v \alpha_v - \frac{1}{2}(\Gamma_{v,v-2} + \Gamma_{v,v+2} \\ & + \tilde{\Gamma}_{v+1,v-1} + \tilde{\Gamma}_{v+1,v+3})\beta_v \\ & + (\Gamma_{v-2,v} \tilde{\Gamma}_{v-1,v+1})^{1/2} \beta_{v-2} \\ & + (\Gamma_{v+2,v} \tilde{\Gamma}_{v+3,v+1})^{1/2} \beta_{v+2} = 0. \end{aligned} \quad (18)$$

Let us focus our attention on eqs. (12c) and (12d) for non-diagonal elements of the density matrix. The special form of the “incoming” rate terms corresponds to the overall correlation of interaction matrix elements [17,18]. For example, the correlation of matrix elements of transitions $v \rightarrow v+2$ at energy k and $v+1 \rightarrow v+3$ at energy $k+1$ can be implied. Such correlation really takes place in our model because the levels (N, v) and $(N, v+1)$ decay to the same bath states $|\epsilon\rangle$, and the matrix elements of interaction (3) differ only by a common multiplier dependent on the number v .

Using the results of ref. [17] we obtain

$$\begin{aligned} & (\Gamma_{v,v-2} \tilde{\Gamma}_{v+1,v-1})^{1/2} \\ & = 2\pi D_{v-2} \langle V_{v,\epsilon;v-2,\epsilon'} V_{v+1,\epsilon;v-1,\epsilon'} \rangle_{\epsilon'} \end{aligned} \quad (19)$$

and

$$\begin{aligned} \Gamma_{v,v-2} &= 2\pi D_{v-2} \langle V_{v,\epsilon;v-2,\epsilon'}^2 \rangle_{\epsilon'}, \\ \tilde{\Gamma}_{v+1,v-1} &= 2\pi D_{v-2} \langle V_{v+1,\epsilon;v-1,\epsilon'}^2 \rangle_{\epsilon'}. \end{aligned} \quad (20)$$

Such relations between the relaxation constants of (12) lead to a form of the spectrum with a full width much less than would be estimated by the Γ_v values. Let us define the Γ_v parameters. From (20) it follows for $\Gamma_{v,v-2}$ that

$$\Gamma_{v,v-2} \propto \langle v | \hat{x}_6^2 | v-2 \rangle^2 \langle \epsilon | \hat{x}_1^2 | \epsilon' \rangle_{\epsilon'}. \quad (21)$$

It is obvious that the main v dependence in (21) is defined by the matrix element $\langle v | \hat{x}_6^2 | v-2 \rangle$. Really, when considering the average occupation numbers for (N, v) and $(N-1, v+1)$ states it can be concluded that for all modes other than ν_6 they change comparatively little. In particular, for an infinite bath the width $\Gamma_{v,v-2}$ would change because of the first multiplier in (21) only. (Compare, for instance, $\Gamma_v \propto v$ for a spontaneously relaxing oscillator.) Consequently only the phenomenological parameter Γ defined by the relation

$$\Gamma_{v,v-2} = \Gamma v(v-1) \quad (22)$$

can be used^{*}. Thus the value 2Γ defines the decay rate $v=2 \rightarrow v=0$. With the same approximation

$$\tilde{\Gamma}_{v,v-2} = \Gamma_{v,v-2}. \quad (23)$$

The dependence of the shift parameters δ_v in (12) and (18) is described by the constants of the intramode (X_0) and the average intermode scalar anharmonicity (X). For the shift we obtain

$$\begin{aligned} \bar{\nu}_v &= \nu_6 + X_0 v + (k-v)X \\ \delta_v &= \nu_{\text{laser}} - \bar{\nu}_v = \nu_{\text{laser}} - \nu_6 - Xk - (X_0 - X)v \end{aligned} \quad (24)$$

^{*} Some times it is erroneously suggested that there might exist a much stronger dependence of Γ and it contains the density of levels D_{v-2} . This is valid only in the sense of writing Fermi's golden rule in the manner of $\Gamma = 2\pi \langle V^2 \rangle D$, yet, the more the overall density of levels, the less is a particular matrix element of interaction with a single bath level. Therefore the dependence on v in (22) can be only defined with the integral interaction and does not comprise D_{v-2} . This point is discussed in ref. [1] (p. 80), in particular.

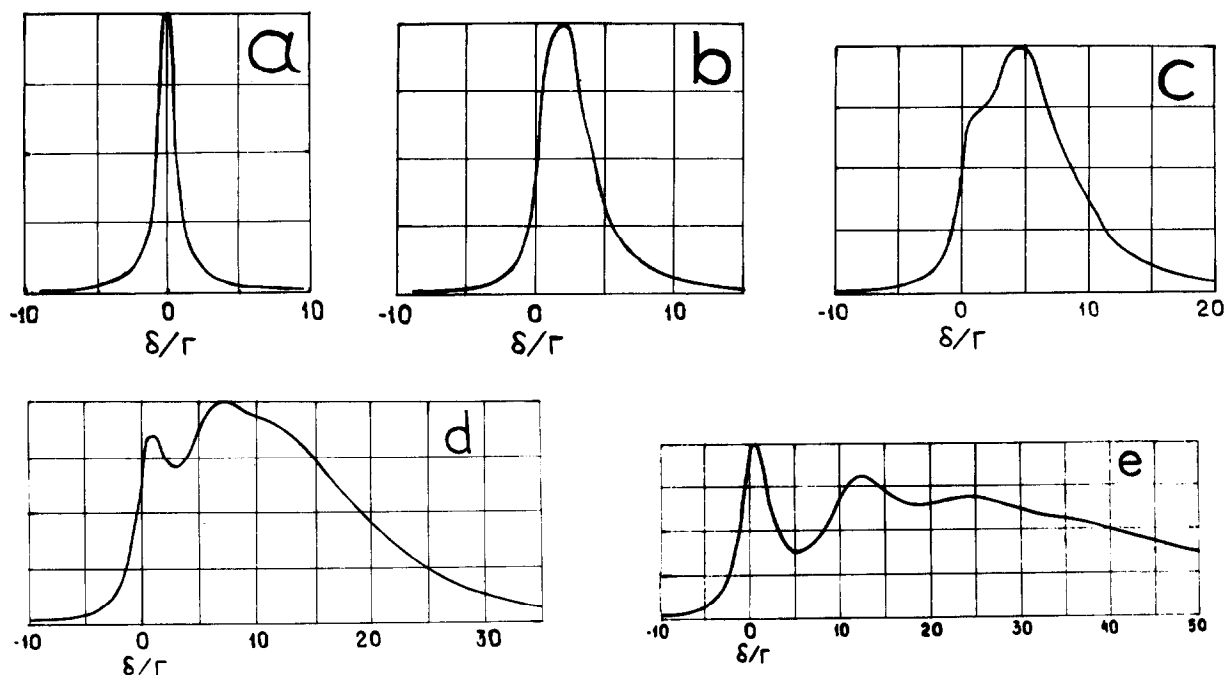


Fig. 10. Model spectra of up transitions normalized by the maxima $X = 0$, and $\Delta X/\Gamma = 0, 1, 2, 4, 10$ for (a)–(e), respectively.

in linear approximation. The constant X can be estimated from the observed hot molecular band approximately at $\nu_{\text{hot}}^{\text{max}} < \nu_{\text{cold}}^{\text{max}}$ (here $\nu_{\text{cold}}^{\text{max}}$ is the centre of linear absorption of non-excited molecules)

$$X \approx (\nu_{\text{hot}}^{\text{max}} - \nu_{\text{cold}}^{\text{max}}) / (\bar{E}_{\text{hot}} - \bar{E}_{\text{cold}}). \quad (25)$$

Now we shall discuss the qualitative consequences of the proposed method of spectrum calculation. The concrete scheme of mode interaction suggested by us is specified by the assumption of the main role of two-quantum transitions ($2\nu_1 \approx 2\nu_6$) leading to the Γ_v dependence (22). For such specific parameters there is no simple analytical solution of the system (18). At the same time computer calculations of the spectra are rather simple. (We restricted ourselves to the total number of equations $V_{\text{max}} = 15$. Further dependence on V_{max} was negligible.)

The difference of anharmonicity constants $\Delta X = X_0 - X$ is one of the crucial parameters for the shape of the spectrum;

$$\delta_v = \delta_0 - \nu \Delta X. \quad (26)$$

In particular, at $\Delta X \gg \Gamma$ the system (18) can be solved by standard perturbation methods. In this case the absorption spectrum has peaks with widths $\Gamma_v + \tilde{\Gamma}_{v+1}$. Another limit ($\Delta X = 0$) leads to one peak of absorption with the width less than Γ_v . Note that such an effect was discussed in refs. [17,26] and is an analogue of the “harmonic oscillator paradox” [26]. The transition from one limiting case ($\Delta X = 0$) to another ($\Delta X \gg \Gamma$) is illustrated by model calculations for the absorption spectra (only up transitions), see fig. 10. For the density of states D_v values calculated for the CrO_2Cl_2 molecule at $E = 19 \times 10^3 \text{ cm}^{-1}$ were used. Let us turn to the following qualitative conclusion. The width of the absorption spectrum cannot be used to uniquely estimate the intramolecular vibrational relaxation (IVR) rate because there is another parameter, i.e. ΔX , which determines the effective width also.

The experimentally observed spectrum depends on both up (induced absorption) and down (induced emission) transitions. Fig. 11 represents the spectra calculated for the CrO_2Cl_2 molecule with different sets of parameters. The constant $X =$

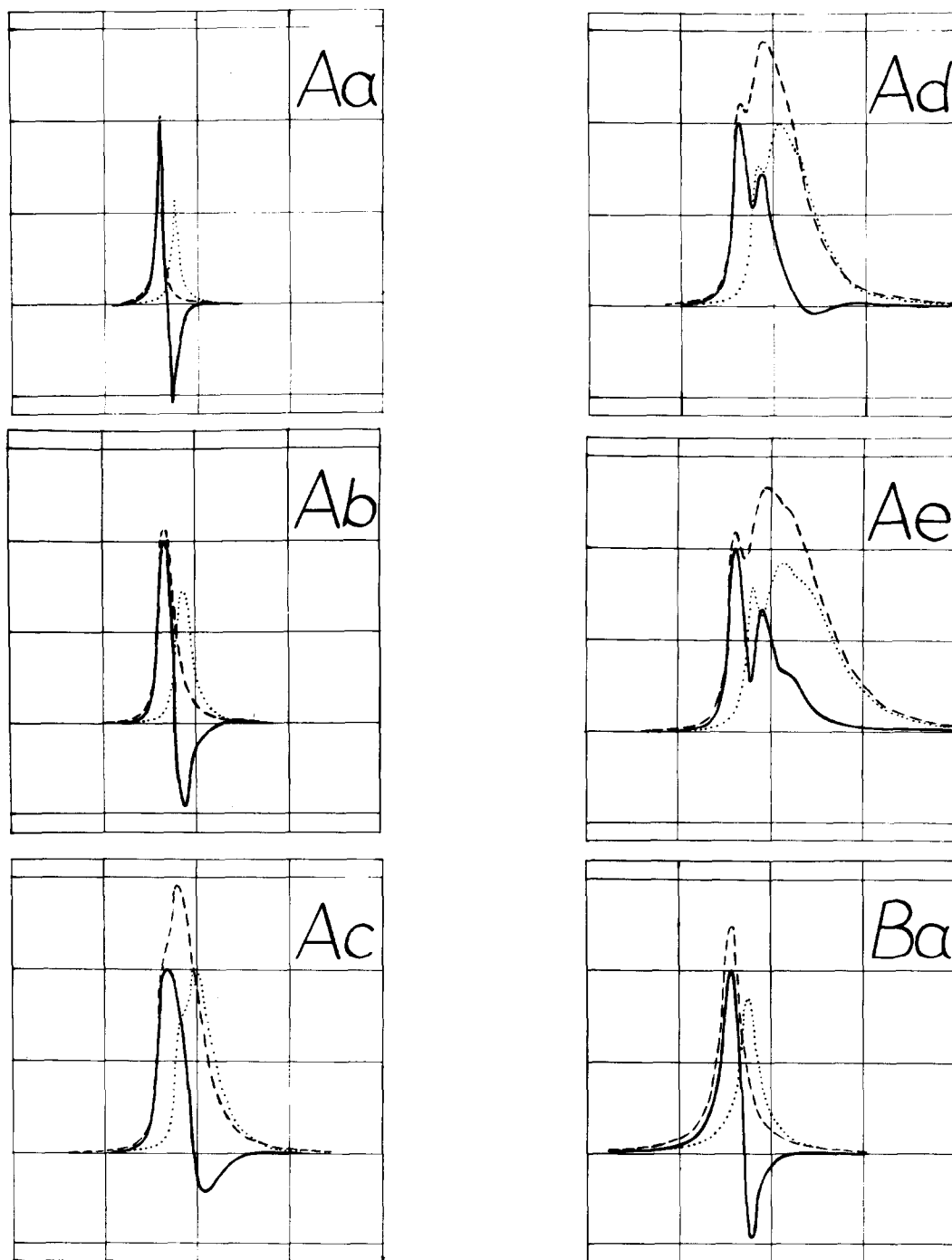


Fig. 11. Calculated spectra for the CrO_2Cl_2 molecule for different sets of parameters. For all curves $X = -37 \text{ cm}^{-1}$. Dashed lines denote up transitions, dotted lines down transitions, solid lines resulted absorption spectra. Capital letters mark the value of the parameter Γ : (A) $\Gamma = 1 \text{ cm}^{-1}$, (B) $\Gamma = 4 \text{ cm}^{-1}$, (C) $\Gamma = 10 \text{ cm}^{-1}$, (D) $\Gamma = 20 \text{ cm}^{-1}$. Small letters mark the values of the parameter ΔX : (a) $\Delta X = 0$, (b) $\Delta X = 1 \text{ cm}^{-1}$, (c) $\Delta X = 2 \text{ cm}^{-1}$, (d) $\Delta X = 3 \text{ cm}^{-1}$, (e) $\Delta X = 4 \text{ cm}^{-1}$. The frequency scales are the same for all figures (from 900 to 980 cm^{-1}). All curves are normalized by the maxima of the absorption spectra. (Continued on next page.)

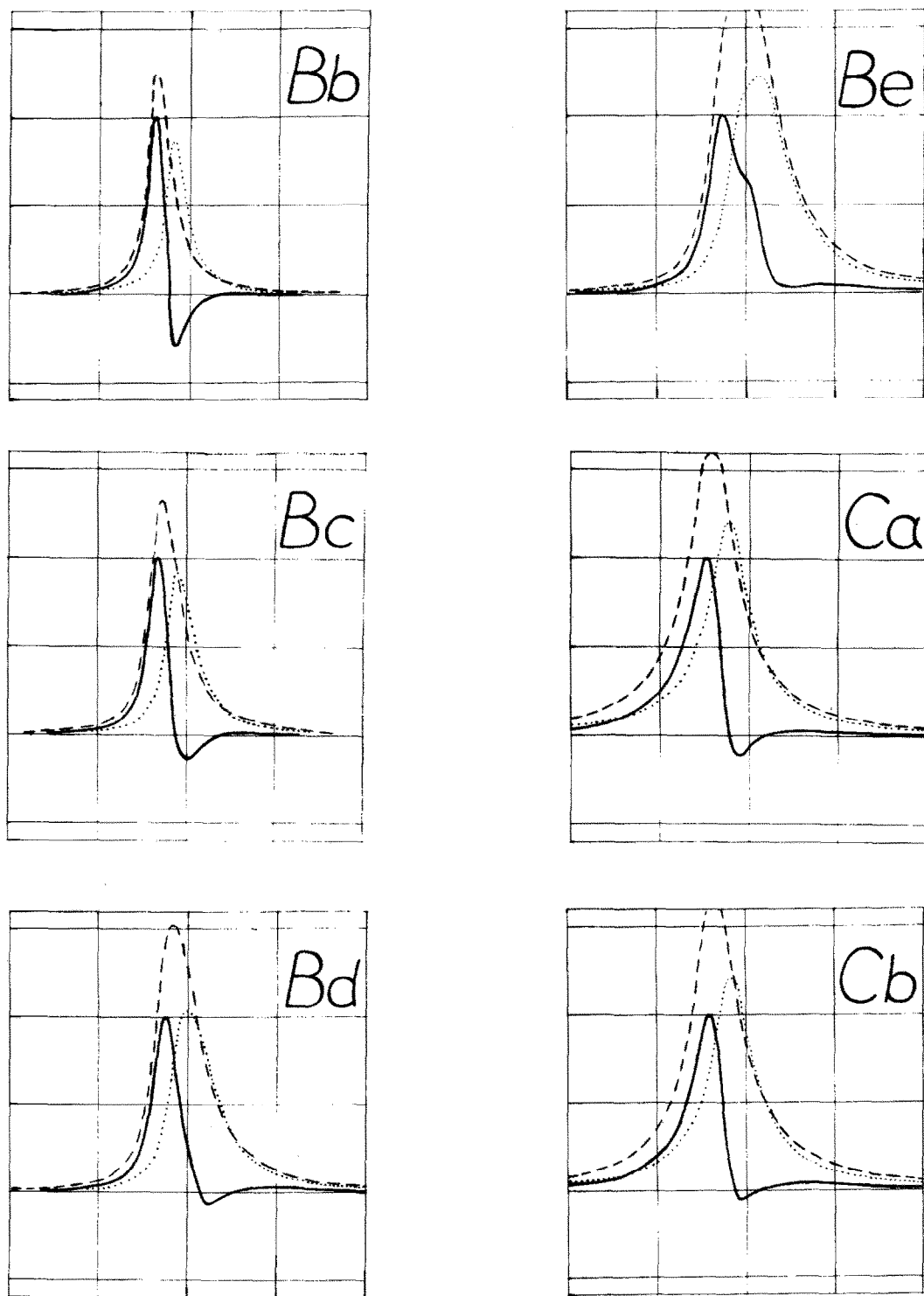


Fig. 11. (Continued.)

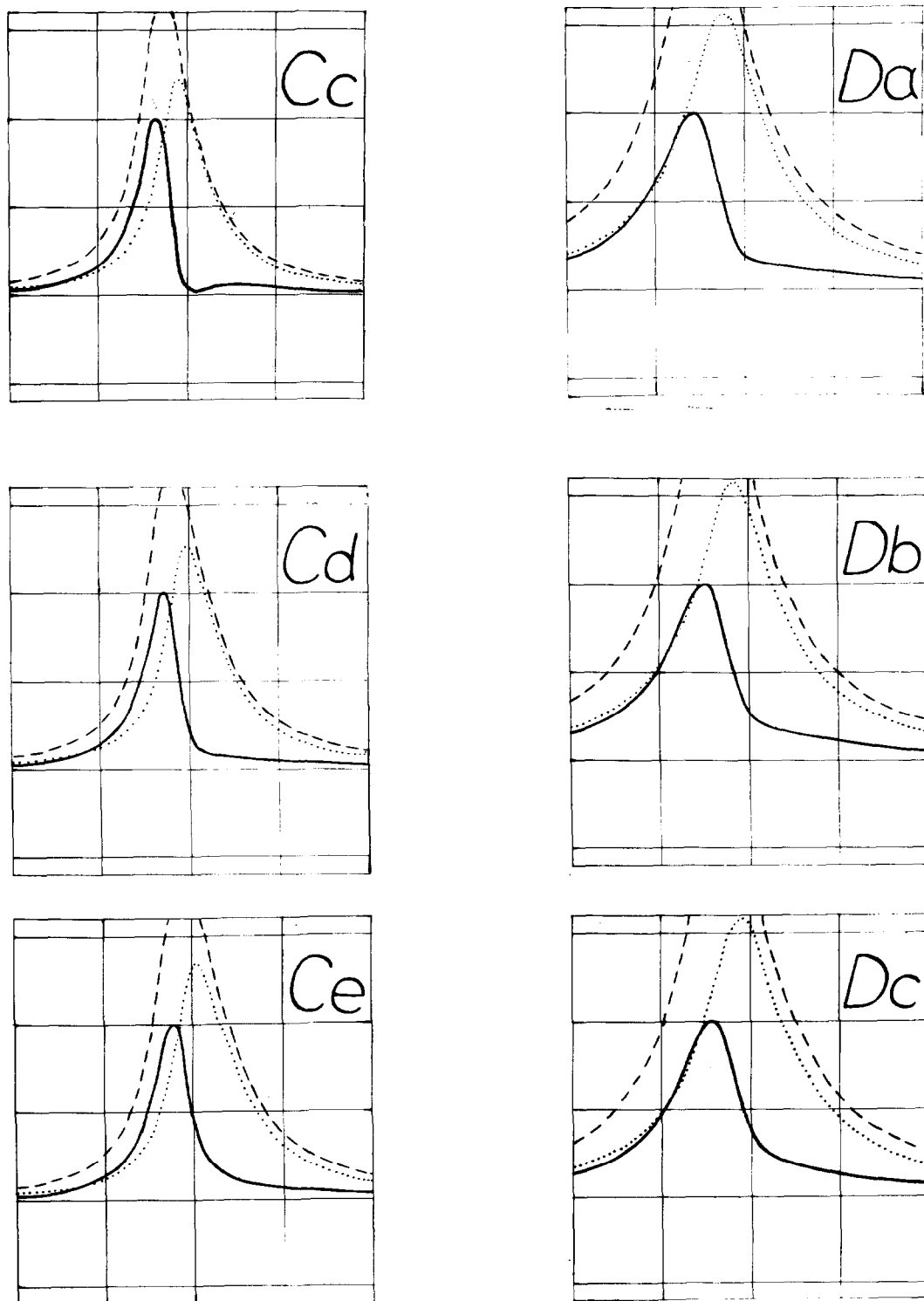


Fig. 11. (Continued.)

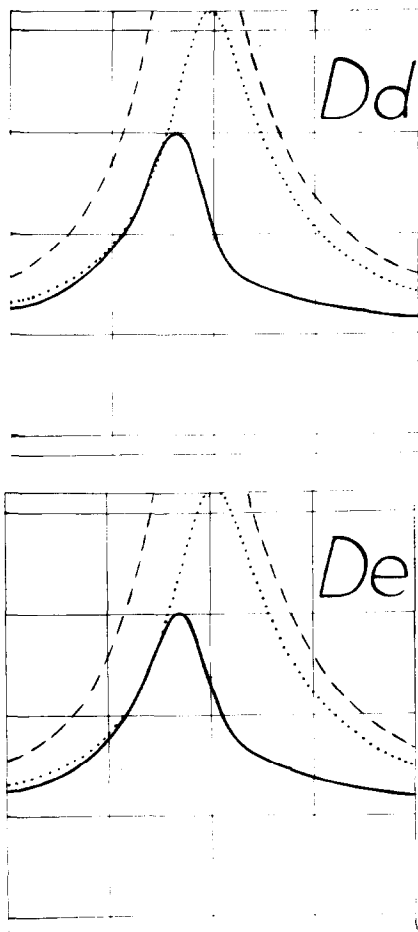


Fig. 11. (Continued.)

-3.7 cm^{-1} (estimated earlier [27]) was chosen so that the induced absorption peak coincides with the experimentally observed peak ($\approx 930 \text{ cm}^{-1}$) in the case when induced emission is shifted (as in fig. 11Aa). From the variants in fig. 11 it is clear that such features of the observed spectrum as the drop and the short-wave pedestal can be explained by the competition of up and down transition in the homogeneously broadened band.

By comparing the different calculated variants of the spectrum with the experimentally observed spectrum one can estimate the values of the phenomenological parameters X , X_0 , and Γ .

Such comparing is illustrated in fig. 12 for

$$\begin{aligned} X &= -3.85 \text{ cm}^{-1}, & X_0 &= -0.7 \text{ cm}^{-1}, \\ \Gamma &= 10 \text{ cm}^{-1}. \end{aligned} \quad (27)$$

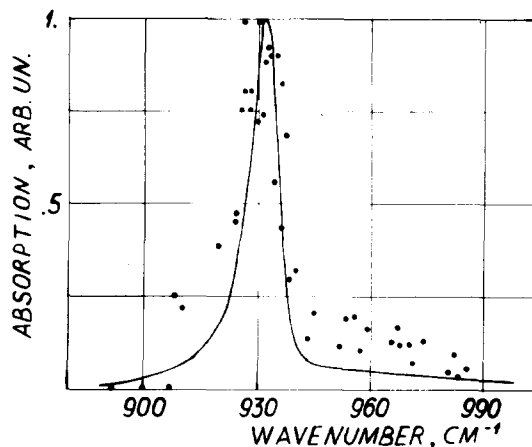


Fig. 12. Comparison of the experimental induced absorption spectrum measured at the minimum delay time of $0.1 \mu\text{s}$ (dots) with the calculated curve ($X = -3.85 \text{ cm}^{-1}$, $X_0 = -0.7 \text{ cm}^{-1}$; $\Gamma = 10 \text{ cm}^{-1}$).

One can see that our model can lead to agreement of theoretical and experimental spectra which is close to quantitative correlation. The parameters X and X_0 are of the typical order of anharmonic shift in middle-size molecules. Now we shall consider the estimation of the parameter Γ . The purpose of this procedure was to express the rates of decay from the mode ν_6 to the bath in terms of anharmonic interaction constants between ν_6 and ν_1 and between the latter mode and the remainder of the molecule.

The use of the markovian approximation (i.e. the rates $\Gamma_{\nu, \nu \pm 2}$ in the equations of type (12)) implies that the matrix element of the \hat{x}_1^2 operator is broadened because of other anharmonic interactions and the value of this broadening $\sigma > V_{1,6}$. To exclude misunderstanding it must be stressed that this broadening really means redistribution of the $\nu_1 \leftrightarrow \nu_6$ interaction over a broad range of both eigenstates. For Γ from (22) we have

$$\Gamma = 2\pi V_{1,6}^2 \overline{\langle \hat{x}_1^2 \rangle^2} D_{0=0}. \quad (28)$$

If the broadening of the matrix element \hat{x}_1^2 is represented by a lorentzian (see appendix) then:

$$\Gamma \approx 2V_{1,6}^2 \langle (v_1 + 1)(v_1 + 2) \rangle \sigma / (\sigma^2 + \Delta^2). \quad (29)$$

The σ value can be estimated assuming that the ν_1

mode is coupled with other ones due to the third-order resonance which are overlapped at the energy of “hot” molecules (see appendix). In this case

$$\Gamma \approx \frac{1}{\pi} \frac{\langle (v_1 + 1)(v_1 + 2) \rangle}{\rho_{\text{res}}} \frac{\bar{\nu} s}{E} \left(\frac{V_{1,6}}{V_3} \right)^2. \quad (30)$$

Here V_3 is the average constant of third-order anharmonic coupling of the ν_1 mode with other ones, $E = 19 \times 10^3 \text{ cm}^{-1}$ is the energy of “hot” molecules. The parameters ρ_{res} , $\bar{\nu}$, and s belong to the “molecule” without ν_6 mode: $\bar{\nu} \approx 370 \text{ cm}^{-1}$ is the average frequency, $\rho_{\text{res}} \approx 1/50 \text{ cm}^{-1}$ is the density of third-order resonance, and $s = 8$ is the number of degrees of freedom. For the excited CrO_2Cl_2 molecule

$$\Gamma \approx 30(V_{1,6}/V_3)^2 \text{ cm}^{-1}. \quad (31)$$

The \hat{x}_1^2 matrix element broadening parameter σ (see appendix, eq. (A.9)) is:

$$\sigma \approx 0.8V_3^2 \text{ cm}^{-1}. \quad (32)$$

The suggested validity of the markovian approximation ($V_{1,6} < \sigma$) leads to the condition (all values in cm^{-1}) that

$$0.8V_3^2 > V_{1,6}. \quad (33)$$

From relation (31) at the Γ value used for a final comparison of calculations and experiment (fig. 12, $\Gamma = 10 \text{ cm}^{-1}$) it follows that

$$V_{1,6} > 0.4 \text{ cm}^{-1}, \quad V_3 > 0.7 \text{ cm}^{-1}. \quad (34)$$

Simplifying formula (29) to (30), the condition $\sigma \geq \Delta$ was used, i.e. from (32) and (4) it follows

$$V_3 \geq 4 \text{ cm}^{-1}. \quad (35)$$

These low estimates do not contradict the usual values of anharmonicity constants. However from (31) and the condition $\Gamma = 10 \text{ cm}^{-1}$ it is evident that

$$V_{1,6} \approx V_3. \quad (36)$$

Being self-critical, it must be said that this result is not so good since the $V_{1,6}$ constant is of fourth-order and V_3 is one of third-order anharmonicity. If the $V_{1,6}$ value is really anomalously

high, then it manifests itself in the spectra of the $\nu_6 = 1 \rightarrow \nu_6 = 2$ transition or in the overtone $\nu_6 = 0 \rightarrow \nu_6 = 2$ transition, and this is available for an independent test. The improper usage of the estimate (30) may be another reason of (36). Indeed a strong condition of the resonance overlapping for the ν_1 mode was used. If that was the case, the estimate (30) is valid with an accuracy of an order of magnitude as the expression $\bar{\nu}_i \approx E/s\nu_i$ was used ($\bar{\nu}_i$ are average occupation numbers of the i th mode).

Probably just the neglect of inhomogeneous broadening is a natural explanation of the disappointing result (36). Then the true homogeneous value of Γ would be less than 10 cm^{-1} and $V_{1,6} \ll V_3$. Convolution of the results with the population distribution of a “hot” ensemble (including rotation transitions) is impossible because it is unknown in our experiment which states from the initially thermally populated ones are excited. Consequently a more accurate future experiment may display the intriguing features of the absorption spectra (see fig. 11) including a possible stimulated gain. Such experiment should involve cold molecules in a jet and probing by a continuously tunable laser.

6. Vibrational relaxation of highly excited CrO_2Cl_2 molecules

Under our experimental conditions a pumping pulse excites approximately 1.5% of CrO_2Cl_2 molecules to a state with energy $1.9 \times 10^4 \text{ cm}^{-1}$. Then the prepared “hot” ensemble of molecules becomes Boltzmann-like during its collisions with unexcited molecules. At the same time, the average energy of the “hot” ensemble decreases since some energy is transferred to other (originally cold) molecules. Fig. 13 shows the dependence of the average excitation level of the “hot” ensemble on the time after the excitation pulse. This dependence was obtained from the induced absorption spectra taken at different delay times (see fig. 7). Such spectra enable one to observe the evolution of the distribution function and to determine the relaxation rate constants.

A comprehensive theory of relaxation of vibra-

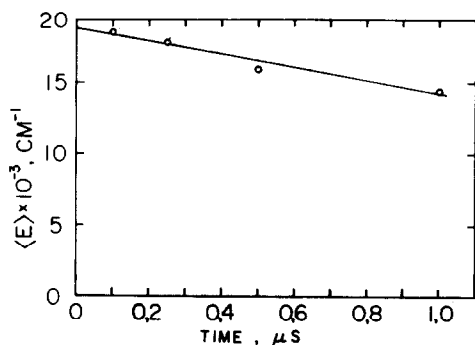


Fig. 13. Time dependence of the average excitation level of CrO_2Cl_2 . The pressure of CrO_2Cl_2 gas in the cell was 0.5 Torr.

tionally highly excited molecules from the original narrow distribution is developed in ref. [28]. The time evolution of the spectra (fig. 7) is in full agreement with theory [28]: the spectra are broadened and shifted to the short-wave side. Such a change of the spectra corresponds to diffusion and drift over the vibrational levels of the QC. The time dependence of the average energy is determined by the following expression [28]:

$$E(t) = E_0 \left[\frac{1}{a} \exp \left(- \frac{a \langle \Delta E(E_0) \rangle}{E_0} Zt \right) - \frac{1-a}{a} \right], \quad (37)$$

where E_0 is the maximum excitation energy, Z is the frequency of gas-kinetic collisions, a is the parameter ($0 \leq a \leq 1$) defining the dependence of the average energy transferred per collision on the excitation energy and

$$\langle \Delta E(E) \rangle = \langle \Delta E(E_0) \rangle (1 - a + aE/E_0). \quad (38)$$

The amount of average energy transferred per collision $\langle \Delta E(E_0) \rangle$ can be obtained by comparing the experimental dependence (fig. 13) with the theoretical one (25):

$$\begin{aligned} \langle \Delta E(E_0) \rangle &= 1300 \pm 200 \text{ cm}^{-1}, & a &= 1; \\ \langle \Delta E(E_0) \rangle &= 1100 \pm 200 \text{ cm}^{-1}, & a &= 0. \end{aligned} \quad (39)$$

The cross section of collisions for CrO_2Cl_2 in this case was taken in a hard-sphere approximation so that the frequency of collisions $Z = 8.2 \times 10^6 \text{ s}^{-1}$ with a pressure of CrO_2Cl_2 gas of 1 Torr. The

accuracy of the experiment as well as the small analysable time range (0.1–1 μs) do not allow to choose a value of the parameter a .

Laser excitation with subsequent internal conversion to the ground electronic state was successful in vibrational relaxations studies [29–31]. The methods of probing were UV absorption [29] and IR-fluorescence [30,31]. The azulene molecule was excited to the energy levels $E_0 = 17500$ and 30600 cm^{-1} , and the average energies transferred per one collision between azulene molecules were 1217 ± 48 and $1425 \pm 31 \text{ cm}^{-1}$ [31], respectively. For the toluene molecule in the state $E_0 = 52000 \text{ cm}^{-1}$ we have $\langle \Delta E(E_0) \rangle = 770 \pm 150 \text{ cm}^{-1}$ with $a < 0.25$ [29].

7. Conclusion

In this work the CrO_2Cl_2 molecule was used to demonstrate the potentialities of a new spectroscopic approach to the study of highly excited vibrational levels in the ground electronic state. This method is not universal as far as the preparation of excited molecules is concerned. It can be applied only to molecules whose electronic states lie at least below the dissociation limit. But for such molecule this method is rather simple and enables one to obtain information on the spectra of transitions from highly excited vibrational states. It must be noted that IR absorption spectroscopy is not the only method of probing the molecules thus excited. Other methods such as IR-fluorescence, spontaneous Raman scattering, and CARS can be used in combination with excitation via a non-radiative transition.

Advantages and disadvantages of these methods are not the topic of this section. However, it should be noted that the combination of IR and Raman probing may yield desirable information about the properties of the spectra of almost all vibrational bands of the molecule. The most interesting feature of the spectra of vibrational transitions from highly excited states seems to be homogeneous broadening. As follows from the theoretical considerations in refs. [16,20,24], this value, generally speaking, is different for different bands. The fuller the set of experimental results, the fuller

the information on intermode interactions in a molecule.

The theoretical analysis presented in section 5 is illustrative and is not claimed to be complete. This is mainly connected with the fact that the value of the inhomogeneous spectral broadening component related to the spread of energies of highly excited molecules is not known. But the experiment shows that the widths of the bleaching contour in the spectrum of the molecules in the lower vibrational levels is smaller than the width of the absorption contour of the excited molecules.

Another shortcoming of the calculation is that the rotational structure of the transitions is not taken into account. It is difficult to overcome this here because the rotational states interacting with the second-harmonic radiation of the Nd:YAG laser are unknown. Besides, as noted in section 5, the adjustment of the results of calculations to the experiment is not quite unambiguous. Ambiguity can be achieved by varying the molecular excitation energy.

In order to obtain experimental results that can be interpreted more precisely, it is necessary to cool the gas (for example, using a supersonic jet) and to use a high-power tunable laser for excitation of the molecules. The spectral width obtained in such an experiment will enable one to conclude whether the excitation energy lies in the region of vibrational quasi-continuum or, in other words, in the region of stochastic vibrational motion [1]. This was assumed in this work without evidence (see the title of the paper). The calculation was carried out under this natural assumption although the lower limit of stochasticity in CrO_2Cl_2 is unknown, and there are just two cases, SF_6 and CF_3I where this boundary was estimated experimentally [32]: $3900 \pm 500 \text{ cm}^{-1}$ for SF_6 and $6000 \pm 500 \text{ cm}^{-1}$ for CF_3I .

At present there is only one method for the spectroscopy of the vibrational quasi-continuum of polyatomic molecules which is an alternative to that realized in the present paper (see also ref. [15]). This is ordinary linear absorption spectroscopy of high-frequency vibrational modes (for example, C–H vibrations). In addition to the papers referred to in section 1 [2–5], where high-

overtone spectra are investigated attention must also be paid to the experiments [33–35] where the spectra of the fundamental bands of the C–H vibration and their overtones in $(\text{CF}_3)_3\text{CH}$ and $(\text{CF}_3)_3\text{C}-\text{C}\equiv\text{C}-\text{H}$ are studied. But linear spectroscopy as a method for studying the vibrational quasi-continuum is suitable only for high-frequency vibrations and (or) very complex molecules with a low boundary of quasi-continuum and its possibilities are limited by attainable vibrational energy. Therefore it is of interest to search for universal methods which would allow preparation of molecules in highly excited vibrational states with a narrow possible energy distribution. It is quite possible that the following possibilities will be realized in the future as a stage preceding spectrum probing together with the method developed in the present work: (1) direct pumping of a high overtone; (2) biharmonic pumping (in particular, via a resonant electronic term [36]); (3) resonant excitation by a powerful IR field when the energy distribution width is negligible; (4) resonant collisional transfer of energy from laser-excited atoms.

Acknowledgement

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Appendix

In section 5 in order to express the phenomenological parameter Γ in terms of molecular anharmonic constants a form of the matrix element $\langle \hat{x}_1^2 \rangle$ “smearing” over the bath levels must be found. It should be noted that this problem is *formally equivalent* to the determination of the ν_1 overtone spectrum in the “molecule” without ν_6 . From the physical point of view $\nu_1 \leftrightarrow \nu_6$ coupling plays the role of a probing field. Then it is convenient to represent all the states of such a “molecule” similarly to the method used for our initial

problem (fig. 9a), i.e. ν_1 is distinguished as the mode of interest from the bath of the remaining "molecule". (This bath does not include ν_1 and ν_6 coordinates.) The scheme of such a level division is shown in fig. 9b. Let us assume linear coupling of the ν_1 mode to the rest of the "molecule" on the account of the third-order anharmonicity. Then the intramolecular relaxation leads to the transitions $v_1 \rightarrow v_1 \pm 1$.

The spectrum of $\langle \hat{x}_1^2 \rangle$ can be determined by the method considered in section 5. The equations similar to (18) are

$$\begin{aligned} & -i\delta_v\beta_v - \frac{1}{2}[\gamma_{v,v-1} + \gamma_{v,v+1} \\ & + \tilde{\gamma}_{v+2,v+1} + \tilde{\gamma}_{v+2,v+3}]\alpha_v \\ & + (\gamma_{v-1,v}\tilde{\gamma}_{v+1,v+2})^{1/2}\alpha_{v-1} \\ & + (\gamma_{v+1,v}\tilde{\gamma}_{v+3,v+2})^{1/2}\alpha_{v+1} = 2i\Omega_v p_v(\text{st}), \\ & -i\delta_v\alpha_v - \frac{1}{2}[\gamma_{v,v-1} + \gamma_{v,v+1} \\ & + \tilde{\gamma}_{v+2,v+1} + \tilde{\gamma}_{v+2,v+3}]\beta_v \\ & + (\gamma_{v-1,v}\tilde{\gamma}_{v+1,v+2})^{1/2}\beta_{v-1} \\ & + (\gamma_{v+1,v}\tilde{\gamma}_{v+3,v+2})^{1/2}\beta_{v+1} = 0, \end{aligned} \quad (\text{A.1})$$

where

$$\Omega_v = \Omega[(v+1)(v+2)]^{1/2}. \quad (\text{A.2})$$

Using the same approximation as for (22) we define

$$\gamma_{v,v-1} = \gamma v. \quad (\text{A.3})$$

In order to obtain an estimated relation, one has to use the approximation

$$d_{v+1}/d_v = \kappa = \text{constant}, \quad (\text{A.4})$$

where the densities of states d_v determine the relations of the $\gamma_{v,v\pm 1}$ parameters:

$$\gamma_{v,v+1}/\gamma_{v+1,v} = d_{v+1}/d_v. \quad (\text{A.5})$$

The overtone spectrum is found from (A.1):

$$I(\delta) = \lim_{\Omega \rightarrow 0} \sum_v i\Omega_v \alpha_v / \Omega^2. \quad (\text{A.6})$$

Using the limit $\delta_v = \Delta = \text{constant}$ it is easy to obtain the required result. By multiplying (A.1) by

Ω_v and summing over v we have

$$I = \gamma(1 - \kappa) / [\Delta^2 + \gamma^2(1 - \kappa)^2]. \quad (\text{A.7})$$

In other words the spectrum of the \hat{x}_1^2 operator in this approximation has a lorentzian form with a hwhm $\sigma = \gamma(1 - \kappa)$.

The introduction of a Boltzman distribution over the v_1 levels ($\kappa = \text{constant}$) is equivalent to the definition of the temperature T :

$$\kappa = \exp(-v_1/T). \quad (\text{A.8})$$

The constant γ can be estimated from the condition of resonance overlapping. When $T \gg \bar{\nu}$, where $\bar{\nu}$ is the average frequency of the molecule without ν_6 , one obtains [24]:

$$\sigma = 2\pi V_3^2 T \rho_{\text{res}} / \bar{\nu}. \quad (\text{A.9})$$

Here V_3 is the average constant of the third-order anharmonicity, ρ_{res} is the density of the resonances including the ν_1 mode. The temperature T can be found from the relation $E \approx sT$ (E is the energy of probed molecules, $s = 8$ is the number of degrees of freedom after the ν_6 mode is excluded). It is of interest that the overtone half-width σ is twice the hwhm of a one-photon transition [24]. At $\sigma > \Delta$ we have the estimate (30).

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