A Contribution to the Investigation of T_2-Relaxation with a Microwave Pulse Spectrometer

Rotational Lines of Ethylene Oxide

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The T_2-relaxation of the $2_{20}-2_{11}$ rotational transition of ethylene oxide in different vibrational states, the ^{13}C-isotope and the perdeuterated species has been investigated by a microwave pulse spectrometer. Qualitative arguments for an explanation of the results in terms of relaxation matrix elements are given.

In a recent paper Mäder et al. [1] reported measurements of T_1- and T_2-relaxation times [2, 2a] of ethylene oxide by using the transient Stark-switch technique. To investigate isotopic species in natural abundance and higher vibrational states it was necessary to use a microwave pulse spectrometer [3] which is at least one order of magnitude more sensitive than our Stark-switch apparatus. As the pulse spectrometer works from 12 to 18 GHz, only the $2_{20}-2_{11}$ transition of ethylene oxide could be measured. The coefficient β of the linear pressure dependence of $1/T_2$ (slope) of the investigated lines is given in Table 1. The frequencies for the excited vibrational states are taken from Yoshimizu et al. [4].

For the measurements we used an ethylene oxide sample from J. T. Baker Chemicals Co. with a purity of 99.7% after vacuum distillation. The necessary A/D conversion of the broadband amplified transient emission signal was carried out in steps of 5 nsec by means of a Biomation 6500 Waveform Recorder. The following averaging was performed by a 1024 channel digital averager (Fabri Tek Model 1072). For the final analysis a Digital Equipment Corp. PDP 11 or Texas Instruments TI 990/10 computer has been used. Some further details on the data analysis and the advantages of the pulse spectrometer compared to the linewidth and Stark-switch methods are given in Reference [3]. An example of a recorded transient emission signal for two different pressures is given in Figure 1. A Fourier transform pair of the ν_c-line of ethylene oxide is given in Figure 2. As can be seen from Table 1 there is no significant dependence of T_2 on isotopic substitution. This is in agreement with results [3] on formaldehyde and sulphur dioxide. In addition the dependence on vibrational state is not significant for the investigated transition. For SO_2 Bestmann et al. [3] found the same result. This indicates that finer details of the rotational spectrum are not reflected by the T_2-relaxation.

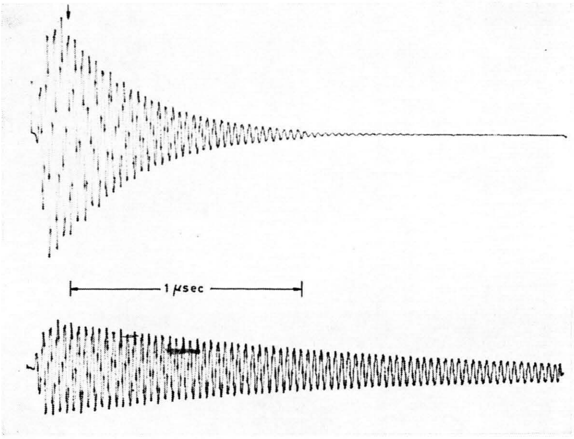

Fig. 1. Transient emission signal of the $2_{20}-2_{11}$ transition of ethylene oxide in the ground state for 16.0 and 5.1 mT and 218 K. To account for initial perturbation the data analysis starts 400 nsec after the end of the polarizing microwave pulse at ↓.

In the following we give some arguments that the existing theory for rotational relaxation may be extended to asymmetric top molecules. Thus the relaxation of asymmetric tops may be related to

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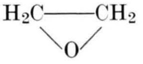
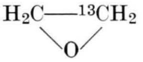
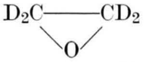
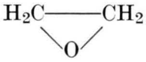
Table 1. Measurement of the pressure dependence of the rotational relaxation time T_2. According to $1/T_2 = \beta p + \alpha$ the slope β is given. Errors are the double standard error of the fit.

Molecule	Transition $j_{k_- k_+} - j'_{k'_+ k'_-}$	Frequency (MHz)	β (MHz/mT)	Temperature (K)
	$2_{20} - 2_{11}$ (G.S.)	15 603.23	0.139 ± 0.002	299
	$2_{20} - 2_{11}$ (ν_b, 892 cm^{-1})	15 238.77	0.140 ± 0.008	299
	$2_{20} - 2_{11}$ (ν_c, 877 cm^{-1})	15 531.11	0.143 ± 0.006	299
	$2_{20} - 2_{11}$ (G.S.)	16 195.96	0.141 ± 0.005	299
	$2_{20} - 2_{11}$ (G.S.)	16 401.71	0.139 ± 0.006	299
	$2_{11} - 2_{02}$ (G.S.)	14 344.07	0.133 ± 0.002	299
	$2_{20} - 2_{11}$ (G.S.)	15 603.23	0.182 ± 0.002	218
	$2_{20} - 2_{11}$ (G.S.)	measured by Stark-switch [17]	0.185 ± 0.001	213

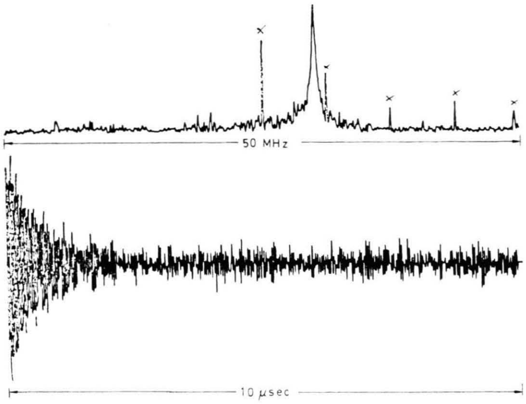


Fig. 2. Fourier transform pair of the $2_{20}-2_{11}$ transition of ethylene oxide in the vibrational state ν_c taken at room temperature and 4 mT. The transient emission signal was recorded by a homemade 1 bit 10 nsec A/D converter and digital averager. x indicates coherent perturbations.

collision processes in a similar way as for linear molecules. One essential approximation for the following is the impact approximation*. According to recent theoretical approaches (see for example Liu et al. [5], Pickett [6], Green [7], Schwendeman et al. [8]) the relaxation times T_1 and T_2 can be correlated under certain assumptions to matrix elements of the relaxation superoperator Λ. These matrix elements can be expressed by elements of the S-matrix, which in turn may be connected in a semiclassical way to the interaction potential $V(t)$. This can be expanded in terms of molecular multipole moments.

For the following we accept the theory of Liu [5] to be a valid description for our investigation (for a different approach see Bottcher [9]).

The eigenstates of an asymmetric top $|j\tau m\rangle$ with $\tau = k_- - k_+$ can be expressed as linear combinations of symmetric top** eigenstates $|jkm\rangle$:

$$|j\,\tau\,m\rangle = \sum_k a_{jk}^{\tau}\,|j\,k\,m\rangle\,. \tag{1}$$

The formalism of Liu et al. which is given for linear molecules can be generalized to asymmetric top molecules by replacing the state vector $|jm\rangle$ by $|jkm\rangle$ and taking proper linear combinations according to (1). To account for the m-degeneracy in symmetric top rotational states $|jkm\rangle$ one has to replace Eq. (4.4) of Liu by (see Ben-Reuven [10], formula (7)):

$$\begin{aligned} &|k_{\rm f}\,j_{\rm f}, k_{\rm i}\,j_{\rm i}; {\rm KQ}\rangle\rangle \\ &\quad= \sum_{m_{\rm f}, m_{\rm i}} (2K+1)^{1/2}(-1)^{j_{\rm f}-m_{\rm f}} \begin{pmatrix} j_{\rm f} & j_{\rm i} & {\rm K} \\ m_{\rm f} & -m_{\rm i} & -{\rm Q} \end{pmatrix} \\ &\qquad \cdot |k_{\rm f}\,j_{\rm f}\,m_{\rm f}, k_{\rm i}\,j_{\rm i}\,m_{\rm i}\rangle\rangle \end{aligned} \tag{2}$$

where $|k_{\rm f} j_{\rm f}, k_{\rm i} j_{\rm i}; {\rm KQ}\rangle\rangle$ represents a Liouville vector of tensorial character KQ [10, 11]. i and f indicate the initial and final states of the molecule under consideration. The expression for the asymmetric top eigenstates can be obtained by taking linear combinations according to (1). As the summation in (2) is only over the m-quantum numbers and the expansion coefficients a_{jk}^{τ} in (1) do not depend on m, there arises no difficulty. It is obvious that the matrix elements of Λ which describe the relaxation of the density matrix ϱ are essentially unchanged for the step from the linear to the asymmetric top molecule. In our experiment the absorption of the microwave radiation takes

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* Other assumptions may be taken from the cited references.

** We use small k for symmetric top and small j for angular momentum quantum number.

place in the absence of external static electric or magnetic fields, that is $1/T_2$ for the relaxation of $\varrho_{\mathrm{fi}}(\mathrm{KO})$* can be expressed similar to Eq. (4.31) of Liu by

$$1/T_2 = Re\, \Lambda^{K}_{\mathrm{fi,fi}} \tag{3}$$

where i and f now indicate asymmetric rotor levels. The special case of $\Delta j = 0$ transitions for asymmetric rotors has to be considered separately for the case of the presence of a static electric field as used in Stark-switch experiments. Results from these experiments are used for comparison. According to (4.11) of Liu, which gives the dipole matrix element for the $\Delta j = 0$ case

$$\begin{aligned}&\langle j\,\tau_{\mathrm{i}}\,m|\,\mu\,|j\,\tau_{\mathrm{f}}\,m\rangle\\ &\quad= -\langle j\,\tau_{\mathrm{i}}(-m)|\,\mu\,|j\,\tau_{\mathrm{f}}(-m)\rangle\end{aligned} \tag{4}$$

we have to use $\varrho_-(j\tau_{\mathrm{i}}, j\tau_{\mathrm{f}})$, to get the polarisation $p(t)$ according to

$$\begin{aligned}p(t) &= \langle j\,\tau_{\mathrm{f}}\,m|\,\mu\,|j\,\tau_{\mathrm{i}}\,m\rangle\,\varrho_-(j\,\tau_{\mathrm{i}}, j\,\tau_{\mathrm{f}})\\ &\quad+ \langle j\,\tau_{\mathrm{i}}\,m|\,\mu\,|j\,\tau_{\mathrm{f}}\,m\rangle\,\varrho_-(j\,\tau_{\mathrm{f}}, j\,\tau_{\mathrm{i}})\end{aligned} \tag{5}$$

with (4.33) of Liu:

$$\begin{aligned}&\varrho_\pm(j\,\tau_{\mathrm{i}}, j\,\tau_{\mathrm{f}})\\ &\quad= \varrho(j\,\tau_{\mathrm{i}}\,m, j\,\tau_{\mathrm{f}}\,m) \pm \varrho(j\,\tau_{\mathrm{i}}(-m), j\,\tau_{\mathrm{f}}(-m))\,.\end{aligned}$$

Liu et al. have shown, that for $\Delta j = \pm 1$ transitions the equation of motion for the density matrix ((4.1) and (4.2) of Liu) may be decoupled by using $\varrho_\pm$. But for $\Delta j = 0$ transitions decoupling is not possible without certain assumptions. This is a consequence of (4) as can be seen from the following equation of motion (for $\Delta j = \pm 1$ transitions compare (4.35) of Liu et al.):

$$\begin{aligned}i\,\frac{\partial}{\partial t}\,\varrho_-(j\,\tau_{\mathrm{f}}, j\,\tau_{\mathrm{i}}) &= \omega_{j\tau_{\mathrm{f}},j\tau_{\mathrm{i}},}\,\varrho_-(j\,\tau_{\mathrm{f}}, j\,\tau_{\mathrm{i}})\\ &\quad- \langle j\,\tau_{\mathrm{f}}\,m|\,\mu\,|j\,\tau_{\mathrm{i}}\,m\rangle\,\varepsilon\cos(\omega t)\\ &\quad\cdot[\varrho_+(j\,\tau_{\mathrm{i}}, j\,\tau_{\mathrm{i}}) - \varrho_+(j\,\tau_{\mathrm{f}}, j\,\tau_{\mathrm{f}})]\\ &\quad- i\,\lambda_{\mathrm{fi,fi}}\,\varrho_-(j\,\tau_{\mathrm{f}}, j\,\tau_{\mathrm{i}}) - i\,\lambda_{\mathrm{fi,if}}\,\varrho_-(j\,\tau_{\mathrm{i}}, j\,\tau_{\mathrm{f}})\,.\end{aligned} \tag{6}$$

In the case of Stark-switch experiments the molecular transition is off-resonant to the microwave radiation during the relaxation period. So we may neglect the influence of the microwave field ε for the relaxation of the density matrix. Then with $\varepsilon = 0$ the equation for the $\Delta j = 0$ transition decouples immediately and we get

$$\begin{aligned}&1/T_2 = \mathrm{Re}\,\lambda^-_{\mathrm{fi,fi}}\,,\\ &\lambda^-_{\mathrm{fi,fi}} = \langle\langle j\,\tau_{\mathrm{f}}\,m, j\,\tau_{\mathrm{i}}\,m|\,\Lambda\,|j\,\tau_{\mathrm{f}}\,m, j\,\tau_{\mathrm{i}}\,m\rangle\rangle\\ &\quad- \langle\langle j\,\tau_{\mathrm{f}}(-m), j\,\tau_{\mathrm{i}}(-m)|\,\Lambda\,|j\,\tau_{\mathrm{f}}(-m), j\,\tau_{\mathrm{i}}(-m)\rangle\rangle\end{aligned} \tag{7}$$

which is different from the $\Delta j = \pm 1$ case given in Ref. [5]. Reversing the analogue of (4.8) of Liu gives:

$$\begin{aligned}&\langle\langle j_{\mathrm{f}}'\,k_{\mathrm{f}}', j_{\mathrm{i}}'\,k_{\mathrm{i}}'; \mathrm{KQ}|\,\Lambda\,|j_{\mathrm{f}}\,k_{\mathrm{f}}, j_{\mathrm{i}}\,k_{\mathrm{i}}; \mathrm{KQ}\rangle\rangle\\ &\quad= \Lambda^{K}_{\mathrm{f'i',fi}} = (2K+1)\sum_{m_{\mathrm{f}}'m_{\mathrm{i}}'}\;\sum_{m_{\mathrm{f}}m_{\mathrm{i}}}(-1)^{j_{\mathrm{f}}'-m_{\mathrm{f}}'+j_{\mathrm{f}}-m_{\mathrm{f}}}\\ &\quad\cdot\begin{pmatrix} j_{\mathrm{f}}' & j_{\mathrm{i}}' & \mathrm{K}\\ m_{\mathrm{f}}' & -m_{\mathrm{i}}' & -\mathrm{Q}\end{pmatrix}\begin{pmatrix} j_{\mathrm{f}} & j_{\mathrm{i}} & \mathrm{K}\\ m_{\mathrm{f}} & -m_{\mathrm{i}} & -\mathrm{Q}\end{pmatrix}\\ &\quad\cdot\langle\langle j_{\mathrm{f}}'\,k_{\mathrm{f}}'\,m_{\mathrm{f}}', j_{\mathrm{i}}'\,k_{\mathrm{i}}'\,m_{\mathrm{i}}'|\,\Lambda\,|j_{\mathrm{f}}\,k_{\mathrm{f}}\,m_{\mathrm{f}}, j_{\mathrm{i}}\,k_{\mathrm{i}}\,m_{\mathrm{i}}\rangle\rangle\,.\end{aligned} \tag{8}$$

That is only the matrix element

$$\langle\langle j_{\mathrm{f}}'\,k_{\mathrm{f}}'\,m_{\mathrm{f}}', j_{\mathrm{i}}'\,k_{\mathrm{i}}'\,m_{\mathrm{i}}'|\,\Lambda\,|j_{\mathrm{f}}\,k_{\mathrm{f}}\,m_{\mathrm{f}}, j_{\mathrm{i}}\,k_{\mathrm{i}}\,m_{\mathrm{i}}\rangle\rangle$$

which we abbreviate as $\Lambda_{\mathrm{f'i',fi}}$, has to be considered. In Appendix A of Liu it is shown, that the matrix element $\Lambda_{\mathrm{f'i',fi}}$ may be expressed in terms of the S-matrix:

$$\begin{aligned}\Lambda_{\mathrm{f'i',fi}} &= \frac{N_2}{2\pi}\sum_{a\,a'}\int \mathrm{d}E_{\mathrm{a}}\,\varrho_{\mathrm{a}}\\ &\quad\cdot(\delta_{\mathrm{f'f}}\,\delta_{\mathrm{i'i}}\,\delta_{\mathrm{a'a}} - S_{\mathrm{f'a',fa}}\,S^*{}_{\mathrm{i'a',ia}})\,.\end{aligned} \tag{9}$$

N_2 denotes the density of the perturbing gas, ϱ_{a} represents the equilibrium distribution of the perturber.

The S-matrix may be expanded in terms of the time evolution operator U (see for example Messiah [12] or Rabitz et al. [13]):

$$\begin{aligned}S &= \sum_{n=0}^{\infty}(-i/\hbar)^n\,S_n\,,\\ S_n &= \lim_{\substack{t\to\infty\\ t'\to-\infty}} U_n(t,t')\,.\end{aligned} \tag{10}$$

U may be expanded in terms of the interaction potential $V(t)$, which is treated as a small perturbation of the time independent Hamiltonian H_0 for the rotation

$$\begin{aligned}&U_0(t,t') = 1,\quad U_1(t,t') = \int_{t}^{t'} V'(t'')\,\mathrm{d}t'',\\ &U_2(t,t') = \int_{t'}^{t} V'(t'')\,\mathrm{d}t''\int_{t'}^{t''} V'(t''')\,\mathrm{d}t'''\,,\end{aligned} \tag{11}$$

and so on with the effective potential

$$V'(t) = e^{iH_0t/\hbar}\,V(t)\,e^{-iH_0t/\hbar}\,.$$

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*$\varrho_{\mathrm{fi}}(\mathrm{KO})$ is an expansion of the density matrix in an irreducible basis according to (4.12) of Liu et al.

For non-overlapping charge distributions of the molecules the interaction potential between two molecules may be expanded (see for example Oka [14] or Gray [15]) in terms of molecular multipole moments*:

$$V(t) = 4\pi \sum_{j_\mathrm{i},\, j_\mathrm{f}} \sum_{m_\mathrm{i},\, m_\mathrm{f}} \sum_{m_\mathrm{i}',\, m_\mathrm{f}'} C_{j_\mathrm{i} j_\mathrm{f}} \begin{pmatrix} j_\mathrm{i} & j_\mathrm{f} & j \\ m_\mathrm{i} & m_\mathrm{f} & m \end{pmatrix} \cdot \frac{Y^*_{jm}\,(\Omega(t))}{R(t)^{j+1}}\, D^{j_\mathrm{i}}_{m_\mathrm{i}' m_\mathrm{i}}\, \hat{M}_{j_\mathrm{i} m_\mathrm{i}'}\, D^{j_f}_{m_\mathrm{f}' m_\mathrm{f}}\, \hat{M}_{j_\mathrm{f} m_\mathrm{f}'}\,. \quad (12)$$

Where $D^j_{m'm}$ is a matrixelement of the rotation operator [17] and $\hat{M}_{jm}$ an effective molecular multipole moment for a certain vibrational state. By insertion of Eqs. (12), (11), (10) and (9) into (3) the relaxation time T_2 can be expressed via the effective interaction potential $V(t)$ in terms of effective molecular multipole moments.

It is known from spectroscopic experience that rotational constants and intramolecular distances in general do not change very drastically with vibronic state, which should imply only slight changes in the molecular multipole moments. In general the alteration is in the order of 1%, the effect of which is believed to be hidden in the experimental uncertainty of the determination of T_2.

A similar conclusion seems to hold for the investigated isotopic species. Our experimental results are in agreement with these qualitative considerations as can be seen from Table 1**.

In Table 1 the $1/T_2$ values of the $2_{20}-2_{11}$ rotational transition of ethylene oxide measured by microwave pulse technique at 218 K and by Stark switch at 213 K, by polarizing the $|m| = 2$ component (Lalowski [18]), are given. Taking into account the small temperature difference, the two values are equal within experimental uncertainty. This means that there is no $|m|$-dependence of the relaxation time T_2 in this case, which is not excluded in principal [5, 8].

Acknowledgements

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* For the vibrational dependence of the interaction potential see Manz [16].

** The linewidth results on HCl of Giraud et al. [19] also show only little dependence on vibrational state.

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