

Fast vibrational relaxation of valence vibrations of the C–H bond in halogenated methane

A. A. Kosterev, A. L. Malinovskii, and E. A. Ryabov

Institute of Spectroscopy, Academy of Sciences of the USSR, 142092, Troitsk

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A fast $V-V'$ relaxation, involving fewer than one collision of the gas particles, of the vibrations of a C–H bond has been observed in CF_3H and CF_2HCl .

1. Numerous studies of vibrational exchange in polyatomic molecules^{1–3} show that the rate constant k of this process can vary over two or three orders of magnitude, depending on the particular properties of the colliding partners. Single-quantum intra-mode $V-V$ exchange is the fastest process in a collision of two molecules. This is a resonant process, has a minimal energy defect, and can occur only as a result of collisions of the gas particles. The rate constant for $V-V$ exchange in the ν_3 mode of CO_2 , for example, is $k_{V-V} = 4.38 \times 10^6 \text{ s}^{-1} \cdot \text{torr}^{-1}$ (≈ 2.5 collisions).¹ The exchange of quanta in the ν_3 mode in CH_3F occurs over about three collisions¹ ($k_{V-V} = 2.7 \times 10^6 \text{ s}^{-1} \cdot \text{torr}^{-1}$). This is apparently one of the highest k_{V-V} values which have been measured for small molecules. The rate of change of the population of certain vibrational states, if they are degenerate, can also exceed the values of k_{V-V} given above, as in the case⁴ of the ν_3 mode of SF_6 . Nevertheless, the rate constant of the elementary event remains roughly the same.⁵ Energy transfer to other modes of the molecule, i.e., $V-V'$ exchange, has a large energy defect and may be accompanied by a change in the occupation numbers of more than two modes simultaneously. As a result, $V-V'$ exchange for a given molecule goes considerably more slowly than resonant $V-V$ exchange, requiring ten or more collisions. As a rule, the corresponding rate does not exceed $k_{V-V'} < 10^6 \text{ s}^{-1} \cdot \text{torr}^{-1}$ (Refs. 1–3), at least for small molecules excited below the quasicontinuum boundary.

In this letter we are reporting the first observation of a very fast $V-V'$ relaxation, which occurs in less than one collision of gas particles. This relaxation of a valence vibration of the C–H bond to other modes of the molecule has been observed in experiments on CF_3H and CF_2HCl .

2. Each of the molecules CF_3H and CF_2HCl has one valence vibration of the C–H bond, ν_1 , with a frequency of 3034.2 cm^{-1} and 3021.3 cm^{-1} , respectively. These vibrations were excited with a picosecond parametric light source, whose output frequency was tuned to the peak of the ν_1 absorption band of the corresponding molecule. The length of the pulse from the picosecond source was $\tau_n \approx 10^{-11} \text{ s}$; its spectral width was $\Delta\nu \approx 30 \text{ cm}^{-1}$. The exciting pulse was focused into a cell holding the gas. The exciting pulse was coaxial with a probing light beam. At the focus, $< 10\%$ of the molecules were excited. Spontaneous Raman scattering was used to probe the excited states. This technique is based on the linear relationship between the integral anti-Stokes Raman signal I_i^{AS} (integral over the states of the mode being probed, ν_i) and

the average occupation number in this mode, $\bar{n}_i: I_i^{AS} \sim \bar{n}_i$. By varying the delay between the exciting and probing pulses, one can observe the variations in the population of the mode being probed or in individual levels of this mode. The measurement technique and the experimental apparatus are described in more detail in Refs. 6 and 7. In the present study, a 2ω pulse from a Nd:YAG laser, with a length $\tau_p = 5 \times 10^{-9}$ s, was used for the probing. The time delay τ_d between the pulses could be varied smoothly; the fluctuations in its value did not exceed $\pm 2 \times 10^{-9}$ s.

3. Figure 1 shows the results on the kinetics of the vibrational relaxation of the ν_1 mode of CF_3H and CF_2HCl . Shown here are the intensities of the anti-Stokes signal, I_1^{AS} , for various values of the product $p\tau_d$ (p is the gas pressure), as τ_d was varied over the range 8–30 ns. The region near the level $\nu_1 = 1$ was singled out from the spectrum, so the results in this figure correspond to the kinetics of the changes in the state population near this level. No significant excitation of higher-lying levels ($\nu_1 > 1$) either by IR light or in the course of the relaxation itself was observed.

The curves in Fig. 1 thus reflect a pumping of energy from the ν_1 mode to other modes of the CF_3H and CF_2HCl molecules. The kinetics of this process is described by an ordinary exponential law. The relaxation time constant found from the slope of the curves is $p\tau = 60 \pm_{10}^{20}$ ns·torr in CF_3H and $p\tau = 30 \pm_5^{10}$ ns·torr in CF_2HCl . The respec-

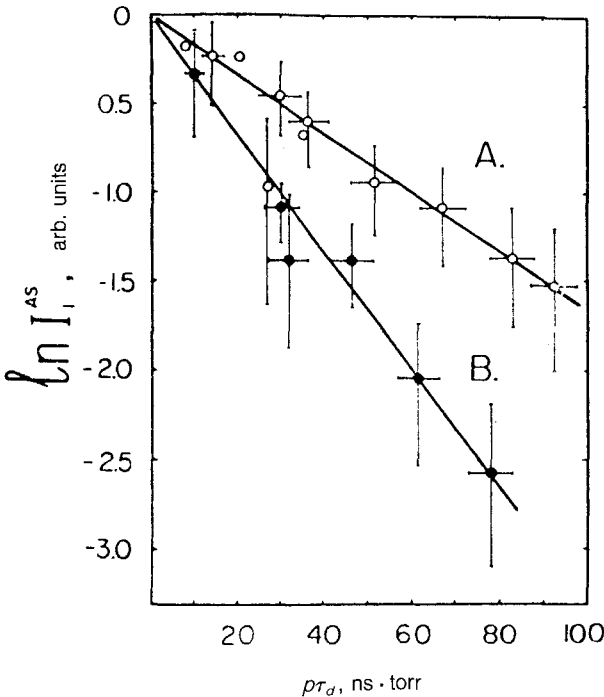


FIG. 1. Intensity of the anti-Stokes Raman signal $I_1^{AS} \sim n_1$, versus $p\tau_d$. A— CF_3H ; B— CF_2HCl .

tive rate constants are $k_{V-V'} = (1.67 \pm 0.38) \times 10^7 \text{ s}^{-1} \cdot \text{torr}^{-1}$ and $k_{V-V''} = (3.33 \pm 0.75) \times 10^7 \text{ s}^{-1} \cdot \text{torr}^{-1}$. The collision rate in CF_3H is $Z = 1.1 \times 10^7 \text{ s}^{-1} \cdot \text{torr}^{-1}$ and that in CF_2HCl is $Z = 1.28 \times 10^7 \text{ s}^{-1} \cdot \text{torr}^{-1}$ (Ref. 8). The energy relaxation from the high-frequency ν_1 mode in CF_3H and CF_2HCl thus occurs in only $\simeq 0.7$ and $\simeq 0.4$ of one collision, respectively.

4. The measured values of the relaxation rate constant of the ν_1 mode in CF_3H and CF_2HCl are more than an order of magnitude higher than the highest known values of this parameter for $V-V'$ relaxation in small molecules. The rate constant for energy transfer from the ν_1 mode to the ν_3 mode in methane, for example, is $(1.2 \pm 0.3) \times 10^6 \text{ s}^{-1} \cdot \text{torr}^{-1}$, while the relaxation of these C-H vibrations to low-frequency deformation modes goes with a constant of⁹ $(0.28 \pm 0.06) \times 10^6 \text{ s}^{-1} \cdot \text{torr}^{-1}$. Our measurements of these constants in CH_4 by the method described above agree within the measurement errors with the data of Ref. 9. This agreement is further evidence for the reliability of the CF_3H and CF_2HCl measurements.

The very high values found for the relaxation constants for CF_3H and CF_2HCl in this study cannot be explained by the existing theoretical models.¹⁻³ Those models ignore the existence of Fermi resonances between different vibrational states, while these resonances are extremely important in the excitation of high-frequency vibrations such as those of the C-H bond. In the IR spectrum of the ν_1 vibration of CF_3H , for example, six additional transitions are observed within an interval of $\pm 30 \text{ cm}^{-1}$. These additional transitions are attributed to a strong Fermi-resonance interaction of the ν_1 vibration with other modes.¹⁰ At least one strong resonance, $\nu_1 \simeq \nu_2 + \nu_7 + \nu_9$, is observed in the CF_2HCl molecule.¹¹ The presence of strong resonances for high-frequency vibrations in CF_3H and CF_2HCl distinguishes these molecules from CH_4 . This distinction, in our opinion, is responsible for the pronounced difference in relaxation constants. The rate constant for $V-V'$ relaxation of the low-lying vibrational levels ν_3 and ν_8 (with a frequency $\sim 1100 \text{ cm}^{-1}$) in HF_2HCl —these levels have no nearby resonances with other modes—is⁶ $k_{V-V'} = (0.7 \pm 0.2) \times 10^6 \text{ s}^{-1} \cdot \text{torr}^{-1}$, or smaller by a factor of nearly 50 than the constant which we measured for the ν_1 mode in the same molecule.

Fermi resonances are known to lead to a mixing of normal modes and to the existence of intramolecular vibrational relaxation in molecules excited above a certain threshold energy (Ref. 7, for example). This threshold for several pentatomic and heptatomic molecules has been found to be⁷ $(5-8) \times 10^3 \text{ cm}^{-1}$. Even below these energies, however, Fermi resonances should play an extremely important role. In particular, they can lead to a rapid redistribution of energy in a transient complex created at the time at which two molecules collide.

We believe that the fast $V-V'$ exchange which we have observed (and which occurs in less than one collision) in the excitation of fairly high-lying vibrational states is more general in nature, not restricted to exclusively CF_3H and CF_2HCl . Fermi resonances should play an important role in this process. We believe that consideration of this circumstance will lead to a quantitative explanation for the observed effect.

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