THE JOURNAL OF
PHYSICAL CHEMISTRY A

Article

pubs.acs.org/JPCA

# Molecular Response Theory in Terms of the Uncertainty Principle

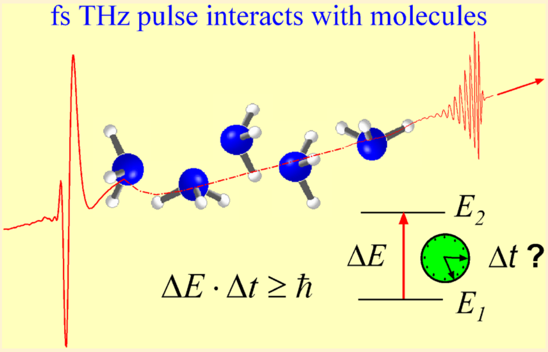
Hermann Harde*

Helmut-Schmidt-University, Holstenhofweg 85, 22043 Hamburg, Germany

Daniel Grischkowsky

Oklahoma State University, Stillwater, Oklahoma 74078, United States

**ABSTRACT:** We investigate the time response of molecular transitions by observing the pulse reshaping of femtosecond THz-pulses propagating through polar vapors. By precisely modeling the pulse interaction with the molecular vapors, we derive detailed insight into this time response after an excitation. The measurements, which were performed by applying the powerful technique of THz time domain spectroscopy, are analyzed directly in the time domain or parallel in the frequency domain by Fourier transforming the pulses and comparing them with the molecular response theory. New analyses of the molecular response allow a generalized unification of the basic collision and line-shape theories of Lorentz, van Vleck–Weisskopf, and Debye described by molecular response theory. In addition, they show that the applied THz experimental setup allows the direct observation of the ultimate time response of molecules to an external applied electric field in the presence of molecular collisions. This response is limited by the uncertainty principle and is determined by the inverse spitting frequency between adjacent levels. At the same time, this response reflects the transition time of a rotational transition to switch from one molecular state to another or to form a coherent superposition of states oscillating with the splitting frequency. The presented investigations are also of fundamental importance for the description of the far-wing absorption of greenhouse gases like water vapor, carbon dioxide, or methane, which have a dominant influence on the radiative exchange in the far-infrared.



## 1. INTRODUCTION

Quantum mechanics has proven to explain all particularities and properties of microsystems, but at the same time it has brought forth some aspects which can no longer be explained in classical terms. Some of these anomalies are the quantization of energy, of momentum, and angular momentum, all in units of Planck's constant, or the uncertainty principle of canonically conjugate variables like position and momentum or energy and time as a consequence of the wave-mechanical nature of matter.

Still one of the rather poorly understood phenomena in quantum physics, particularly in atomic and molecular spectroscopy, is how fast molecules will respond to an external excitation and molecular transitions between different energy states or substates can take place. Some first but still restricted insight into this molecular response we could derive by studying the propagation of femtosecond (fs) THz pulses in dense molecular vapors by means of the powerful technique of THz time domain spectroscopy (THz-TDS).[1−4] To explain all details of such measurements, it was found necessary to expand the classical collision theories of Lorentz[5] and van Vleck–Weisskopf[6] by explicitly including a time response of molecules orienting to an external field in the presence of collisions.

This empirically developed molecular response theory (MRT)[2,3] allowed precise modeling of the THz pulse reshaping in vapors, or after Fourier transforming the pulses into the frequency domain, accurate determination of the absorption and dispersion out to the far wings of the molecular transitions. From simulations with this new MRT, we could derive response times for different molecules between 80 and 220 fs,[2−4] depending on the moment of inertia of the molecules.

In this contribution, we present an extended analysis of some previous and also new THz-TDS measurements for the methyl halides, for trifluorine methane ($CHF_3$) and for ammonia ($NH_3$) with the objective to derive an advanced understanding of the molecular response and transition time after an external excitation.

In addition to the fundamental considerations described above, the far wings of the molecular transitions of the greenhouse gases of water vapor ($H_2O$), carbon dioxide ($CO_2$), methane ($CH_4$), and nitrous oxide ($N_2O$) have an important effect on the radiative exchange. For accurate thermal equilibrium calculations the line-shapes must be accurately known over a broad frequency range extending to the end of the far wings.

Here we obtain a physically consistent line-shape molecular response theory for the rotational resonances, which smoothly

**Received:** June 20, 2015
**Revised:** July 20, 2015
**Published:** August 4, 2015

DOI: 10.1021/acs.jpca.5b05909
*J. Phys. Chem. A* 2015, 119, 9085−9090

connects the near-resonance region, well described by the van Vleck−Weisskopf theory, to the Lorentz line-shape in the far wings.

## 2. FUNDAMENTALS OF MOLECULAR RESPONSE THEORY

The theoretical concept applied to analyze THz-TDS measurements of symmetric top molecules has already previously been described.[2−4] In THz-TDS, two electromagnetic pulse shapes are measured, the input (reference) pulse and the propagated pulse, which has changed shape due to its passage through the sample under study. Consequently, via Fourier analyses of the input and propagated pulses, the frequency dependent absorption and dispersion of the sample can be obtained. Owing to the broad bandwidth of the THz pulses a spectral range extending from less than 100 GHz up to more than 5 THz can be investigated.

For optical and infrared transitions, it is well-known that the simple Lorentzian line-shape[5] provides excellent agreement with experiment, particularly for the central region of absorption lines. However, when the frequencies are reduced to those of the microwave or far-infrared region, and under conditions when a line width becomes comparable with the transition frequency, the absorption profile of a collision broadened line is better represented by the van Vleck−Weisskopf line-shape.[6] Also for the limiting case of zero transition frequency the absorption and dispersion is described by the van Vleck−Weisskopf theory, which then converges to the Debye theory.[7]

The difference between the Lorentz and van Vleck−Weisskopf theory is that the response of a molecule to an external field is only considered in its two limiting cases. While Lorentz assumed that directly after a collision molecules are oriented randomly with respect to the driving field and therefore no macroscopic polarization in the sample will be found, van Vleck and Weisskopf applied Boltzmann's statistics, assuming instantaneous realignment during a collision such that the molecules are oriented as to have a low energy in the field.

A distribution in accordance with the Boltzmann law can be expected when the molecular response is short compared to an oscillation cycle of the field, but when this frequency becomes faster than the molecular orientation, thermalization cannot be established over the collision, and the original approximation of Lorentz is more realistic. The frequency range where the transition between these basic theories occurs indicates the duration of the molecular response. This range is completely covered by the spectrum of the THz pulses and therefore can be investigated by THz-TDS.

In this context, it should be noticed that any redistribution of molecules to the peak THz electric field, which is less than 20 V/m, can only be expected in the presence of collisions, since they are inducing sublevel transitions and thereby allow for changes of the orientation of a molecule.

It might be tempting to associate an orientation time with the duration of a molecular collision, but as defined mathematically below, such orientation reflects the molecular response during a collision. So, the estimated duration of a collision, as obtained from the collision cross-section and thermal velocity, is of the order of 1 ps, while any orientation of molecules during a collision is expected to be much faster, for example, for ammonia molecules it is about 1 order of magnitude shorter. In addition, the wing absorption of van Vleck−Weisskopf theory is particularly sensitive to state changing (diabatic) collisions causing any orientation of the molecules to the external field,[6] while the full line width of a rotational line is additionally determined by phase changing (adiabatic) collisions.

From the above discussion, it is obvious that a more inclusive line-shape theory, which is applicable over the full spectral range, explicitly needs to include the temporal response of molecules to the field. We could derive such a molecular response theory (MRT),[2,3] which considers a time dependent and therefore also frequency dependent extra polarization of the vapor, and which explicitly emanates from a thermalization of dipoles to the impressed field over the collision duration time. We assume this polarization to increase as $\Delta P_{\mathrm{th}}(t,t_0)(1 - \mathrm{e}^{-\vartheta/\tau_{\mathrm{C}}})$ (see ref 2), where $\Delta P_{\mathrm{th}}(t,t_0)$ is the maximum polarization attainable over the time evolution $\vartheta$ of a collision, $t_0$ is the time of a last collision, and $\tau_{\mathrm{C}}$ is the molecular response time. Since the response of molecules is observed as this extra polarization and results in an orientation of the dipoles to the field, we also designate the molecular response time as orientation time.

With the probability $(1/\tau_{\mathrm{C}})\mathrm{e}^{-\vartheta/\tau_{\mathrm{C}}}\mathrm{d}\vartheta$ for a molecule of becoming aligned to the field within a time increment $\mathrm{d}\vartheta$, the effective polarization in an alternating field then can be found by multiplying $\Delta P_{\mathrm{th}}$ by this probability and integrating over the collision duration time. As long as this time is short compared to the mean time $\tau$ between collisions, the interactions over the collisions can be considered to be independent from the time between collisions. Then the effective change in polarization is found as[2]

$$\Delta \mathbf{P}(t, t_0) = \frac{1}{\tau_{\mathrm{C}}} \int_0^{\infty} \Delta P(t, t_0 + \vartheta) \mathrm{e}^{-\vartheta/\tau_{\mathrm{C}}} \, \mathrm{d}\vartheta \tag{1}$$

Since collisions occur at random with a mean interval $\tau$, this polarization has further to be averaged over the various times of last collisions, where the probability, that a collision was in the interval $(t_0 - \mathrm{d}t_0, t_0)$, is $(1/\tau)\mathrm{e}^{-(t-t_0)/\tau}\,\mathrm{d}t_0$. Therefore, eq 1 is multiplied by this probability and integrated over $t_0$ from $-\infty$ to $t$.

In the frequency domain, the magnitude of this extra polarization is determined by the frequency detuning of the field from the transition frequency compared to the reciprocal of the molecular response time $\tau_{\mathrm{C}}$, and it modifies the absorption and dispersion of the vapor giving rise to small corrections in the wing of a spectral line. The faster the response of molecules, the more these contributions are shifted to the far wing of a line up to the limit of instantaneous response which is the van Vleck−Weisskopf case.

The unified line-shape function $g_\alpha(\omega, \omega_{\mathrm{JK}})$ for absorption on a rotational transition as derived from MRT can be calculated as (see ref 2):

$$\begin{aligned} g_\alpha(\omega, \omega_{JK}) = {} & \frac{\Delta\omega_J}{(\omega - \omega_{JK})^2 + (\Delta\omega_J/2)^2} f_\alpha^+ \\ & - \frac{\Delta\omega_J}{(\omega + \omega_{JK})^2 + (\Delta\omega_J/2)^2} f_\alpha^- \end{aligned} \tag{2}$$

which differs from the standard Lorentzian form by being multiplied by additional shape factors, the switching functions $f_\alpha^+$ for the positive resonance term and $f_\alpha^-$ for the "negative" frequency resonance term with

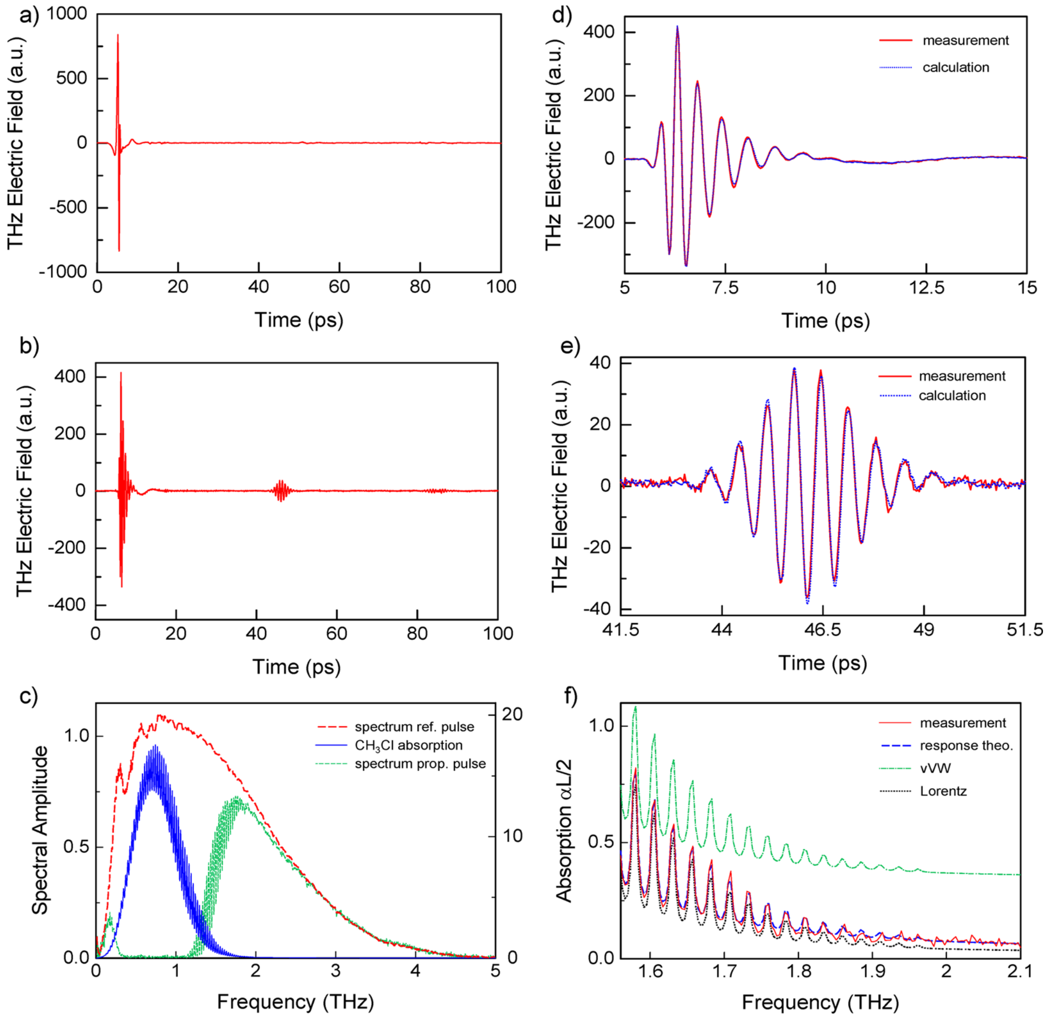


**Figure 1.** (a) THz reference pulse, (b) propagated pulse through 1000 hPa, 22.5 cm long methyl chloride vapor, (c) amplitude spectrum of reference pulse (dashed red) compared with calculated absorption in 1000 hPa methyl chloride (solid blue) and spectrum of propagated pulse (short dashed green), (d) measured main pulse on magnified scale (solid red) compared with MRT (dotted blue), (e) measured first echo on magnified scale (solid red) compared with MRT (dotted blue), and (f) experimental far wing absorption (solid red) compared with MRT (dashed blue), van Vleck−Weisskopf theory (dash dotted green), and Lorentz theory (dotted black).

$$f_\alpha^\pm(\omega, \omega_{JK}) = 1 - \frac{\omega_{JK} \mp \omega}{\omega_{JK}} \cdot \frac{1 + \Delta\omega_J \tau_C/2}{1 + (\omega_{JK} \mp \omega)^2 \tau_C^2} \qquad (3)$$

The general line-shape function $g_k$ $(\omega, \omega_{JK})$ for dispersion is found as[2]

$$g_k(\omega, \omega_{JK}) = 1 - \frac{\Delta\omega_J^2}{8\omega_{JK}}\left[\frac{(\omega_{JK} + \omega)}{(\omega_{JK} - \omega)^2 + (\Delta\omega_J/2)^2} f_k^+ + \frac{(\omega_{JK} - \omega)}{(\omega_{JK} + \omega)^2 + (\Delta\omega_J/2)^2} f_k^-\right] \qquad (4)$$

with the switching functions[2]

$$f_k^\pm(\omega, \omega_{JK}) = 1 - \frac{\omega_{JK} \mp \omega}{\omega_{JK}} \cdot \frac{1 - 2(\omega_{JK} \mp \omega)^2 \tau_C/\Delta\omega_J}{1 + (\omega_{JK} \mp \omega)^2 \tau_C^2} \qquad (5)$$

In these equations, $\omega_{JK}$ represents the resonance frequency of a rotational transition from $J \rightarrow J + 1$, $\Delta K = 0$ with $J$ as the rotational and $K$ as the projection quantum number, and $\Delta\omega_J$ is the $J$ dependent FWHM angular frequency line width, which is assumed to be identical for different $K$ transitions.

So, the general line-shape functions $g_\alpha(\omega, \omega_{JK})$ and $g_k(\omega, \omega_{JK})$ are controlled via the shape factors $f_{\alpha,k}^\pm(\omega, \omega_{JK})$ by the response time $\tau_C$, which defines the transition between the two basic line-shapes and describes the admixture of a van Vleck−Weisskopf profile to a Lorentzian as a function of the frequency detuning from resonance. An inspection of the switching functions shows that in the limit $(\omega_{JK} \mp \omega)^2\tau_C^2 \gg 1$, $f_\alpha^\pm \rightarrow 1$, and the generalized line-shape function becomes the well-known Lorentzian for absorption, while $f_k^\pm \rightarrow 1 + 2(\omega_{JK} \mp \omega)/(\omega_{JK}\Delta\omega_J\tau_C)$. Conversely, when $(\omega_{JK} \mp \omega)^2\tau_C^2 \ll 1$, $f_{\alpha,k}^\pm \rightarrow \pm\, \omega/\omega_{JK}$ and the van Vleck−Weisskopf line-shape is obtained.

For the sake of completeness, it should be mentioned that in symmetric top molecules due to molecular tunneling additional transitions between the two configurations of symmetry, + and − (reflectance at the symmetry plane) take place, which define the inversion spectrum and obey the selection rules $+ \leftrightarrow -$, $\Delta J = 0$, $\Delta K = 0$ for all $J$,$K$-levels with $K > 0$.[8] However, for $NH_3$, these inversion transitions fall in the microwave region, and for the methyl halides as well as for $CHF_3$ the transition frequencies are almost zero, so that they are not directly excited by the THz pulses. Only due to pressure broadening and collision induced alignment of the molecules to the THz field a smaller background absorption, extending up to frequencies in the far-infrared, is expected but can well be neglected for the further considerations. For details of inversion line-shapes with transition frequencies $\omega_i \rightarrow 0$, as derived from MRT, see ref 3.

## 3. ANALYSIS OF THz-TDS MEASUREMENTS

As an example of THz-TDS and its analysis by MRT, in Figure 1 we present a measurement on methyl chloride vapor, which clearly demonstrates the main features of the THz pulse propagation in dense vapors of symmetric top molecules. For details of the experimental setup, see refs 1−4, 9, and 10. The pulses pass through a 22.5 cm long vapor cell which can be evacuated to measure the reference THz pulse, which is displayed in Figure 1a. This pulse essentially consists of a single cycle and can be monitored with a S/N ratio of better than 1000:1.

The corresponding amplitude spectrum, obtained by a numerical Fourier transform of Figure 1a, shows a bandwidth extending well beyond 4 THz. It is displayed in Figure 1c as a dashed red graph in direct comparison with the calculated room-temperature methyl chloride rotational band as solid blue line. Almost all of the polar molecules have their rotational absorption lines within this frequency range and therefore can be investigated with THz pulses.

When the cell is filled with the vapor, in this case with 1000 hPa methyl chloride, the transmitted pulse changes to that shown in Figure 1b. The excitation pulse is strongly attenuated and reshaped due to the absorption and dispersion in the vapor, and it is followed by a series of coherent transients, which appear every 40 ps as commensurate echoes[11−13] on the free induction decay. These coherent transients originate from the synchronous excitation of the molecular ensemble over the whole rotational band structure, which is characterized by an almost constant frequency spacing between adjacent rotational lines. After their excitation, the molecules are freely oscillating on individual rotation frequencies with the consequence that the individual oscillators are periodically dephasing and rephasing. This appears with a beat frequency given by the frequency spacing between adjacent rotational lines and results in the formation of a macroscopic polarization and the re-emission of the periodic echoes. At a pressure of 1 atm, these coherent transients are rapidly decaying due to collisional broadening of the lines, and at this pressure they can only well be identified up to the second echo.

The Fourier transform spectrum of the propagated pulses is also shown in Figure 1c as the short dashed green graph. Between 0.3−1 THz, the vapor is completely opaque for the THz radiation, even in the troughs due to the strongly overlapping line wings at this pressure. Only below 0.3 THz and in the high frequency wing of the rotational band the vapor gets more and more transparent. Particularly the high frequency range is of interest for the further analysis.

The reshaped pulse at 1000 hPa pressure is shown on an expanded time scale as solid red line in Figure 1d and compared to MRT (dotted blue curve). The agreement is excellent, and both lines completely overlap. The first echo, also displayed as a double plot of measurement and simulation in Figure 1e, has been stretched out and appears as a simple wavepacket.

Measurement of the amplitude absorption on the high frequency wing is compared in Figure 1f directly with that calculated from the van Vleck−Weisskopf line shape, the Lorentz shape and the MRT using a collision induced response time of $\tau_C$ = 225 fs.

The calculation based on MRT (dashed blue line) completely overlaps the measured data (solid red graph) on the far wing, while the absorption using the van Vleck−Weisskopf profile (upper dash dotted green curve) is clearly too large and that calculated with a Lorentzian profile (lower graph, black dotted line) is too small. It is clear that the actual absorption falls between that predicted from the van Vleck−Weisskopf and Lorentz theories. The overlap of experiment and theory confirms the validity of MRT and clearly demonstrates its applicability between the two limiting cases of the Lorentzian and van Vleck−Weisskopf theories. Variation of the fitting parameters indicate an uncertainty of about 15% for the response time $\tau_C$, which to first order is found to be independent of the vapor pressure or temperature.

## 4. DISCUSSION OF RESULTS

From our earlier investigations, it was found that the response of molecules colliding in the presence of an electric field is faster for lighter molecules, and from a simple model it is expected that this scales proportional with the moment of inertia along the principal axis. We have investigated this in more detail and performed systematic studies on a series of symmetric top molecules with different moments of inertia. This includes all methyl halides, the molecule trifluorine methane, and ammonia.

The respective response times $\tau_C$ as derived from an analysis of the measurements with the MRT are plotted in Figure 2 as a function of the moment of inertia of the different molecules. The data for $NH_3$ and $CH_3F$ originate from our earlier investigations; the response times of the other molecules were derived from an analysis of new measurements published in ref 10.

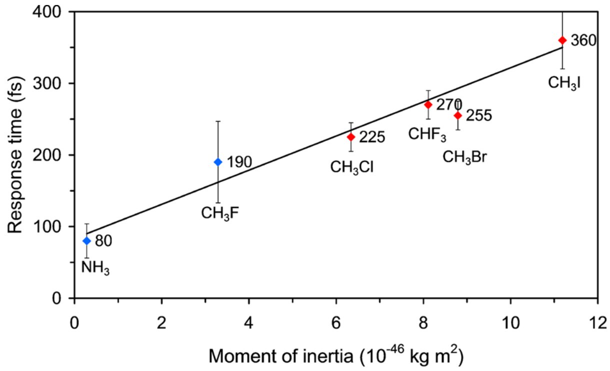


**Figure 2.** Molecular response time of some symmetric top molecules as a function of the moment of inertia along the principal axis.

Except for the methyl bromide case, all data fit well within their error bars to a regression line and confirm an expected increase of $\tau_C$ with the moment of inertia. However, this plot does not explain the time scale on which an orientation of a molecule to the THz electric field can take place in the presence of collisions.

More insight into this response can be derived when a molecule is characterized by an average rotational frequency $\omega_C$, for example, using the maximum or the core area of the rotational band structure, and having in mind that, roughly speaking, this average frequency scales inversely with the

DOI: 10.1021/acs.jpca.5b05909
J. Phys. Chem. A 2015, 119, 9085−9090

moment of inertia of a molecule. Then in an appropriate reference system a molecule can be described as to have an "uncertainty" in its energy, which is given by the average rotational level splitting $\Delta E = \hbar\omega_C$.

In Figure 3, we have plotted the response times of the different molecules as a function of the center frequency, in this case defined by the maximum of the continuous absorption caused by the overlapping wings between the rotational lines. For $CH_3Cl$, for example, this is found as *0.71 THz* (see Figure 1c, lower maximum of absorption spectrum); for $NH_3$ with a much broader spectrum than the THz pulse spectrum, an average over the lines within the pulse spectrum is used. Except for $CHF_3$, the response times now fit to a hyperbolic curve shown as solid pink line.

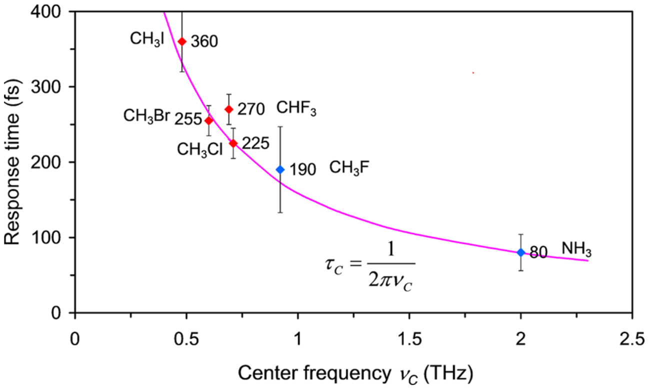


**Figure 3.** Molecular response time of some symmetric top molecules as a function of the center frequency (maximum of the continuous absorption) of the respective rotation band. The solid pink graph is defined by the uncertainty principle eq 7.

This hyperbolic just represents Heisenberg's uncertainty principle[14]

$$\Delta E\Delta t = \hbar\omega_C\Delta t = \hbar \tag{6}$$

where $\Delta E$ is the average energy spacing of adjacent rotational states, $\omega_C$ is the average (center) rotational transition frequency, $\hbar = h/2\pi$ is Planck's constant, and $\Delta t$ is a minimum uncertainty in specifying an exponentially evolving temporal event with respect to a level splitting of $\Delta E$.

The coincidence of the experimentally derived response times $\tau_C$ with the uncertainty relation indicates that this time response can well be represented by the inverse of the center frequency of the rotational band structure of a molecule with

$$\tau_C = 1/\omega_C = 1/2\pi\nu_C \tag{7}$$

At the same time, this means that in terms of MRT the observed orientation of molecules to the THz electric field takes place within the shortest time interval possible for this process and that this orientation which happens in combination with a rotational transition, can well be resolved with the technique of THz-TDS measurements.

Equation 7 defines a response of the molecules which in agreement with MRT can be understood as an average value, at least for the considered rotation band, from which the center frequency $\omega_C$ as an average over the individual rotational transitions was derived. Such a mean response time is expected to represent quite well the experimental data, since the extra absorption originating from the orientation of the molecules also can only be monitored as a superposition of all rotational transitions in the high frequency wing of the absorption band.

An even more sophisticated theory, however, may also distinguish between different response times for the individual transitions in a similar way as it is differentiated between different line widths; and as a consequence of the uncertainty principle the respective response times might just be replaced by the reciprocal of the respective transition frequency of a line. Since the response theory was already formulated as a line-shape correction for each individual transition, in eqs 3 and 5, $\tau_C$ can easily be substituted by $\tau_{JK}$ with

$$\tau_{JK} = 1/\omega_{JK} = 1/2\pi\nu_{JK} \tag{8}$$

A simulation in this way reproduces the measured pulse structures and spectra of the measurements for the investigated molecules extremely well. Only small improvements of the fits can be achieved when multiplying the individual response times of a molecule with a common factor close to one. As an example, the response times of the different molecules as derived from such fits to the measurements are displayed for the $J = 0 \rightarrow 1$ transition in Figure 4. They show only minor deviations from the solid pink graph which represents the theoretical limit for the response of molecules on the lowest rotational line with transition frequency $\nu_{J=0} = 2B_V$, where $B_V$ is the rotational constant of a molecule along the principal axis. For transitions with larger splitting frequencies, the appropriate response is faster, so that the average over the total rotation band is just well reflected by $\tau_C$.

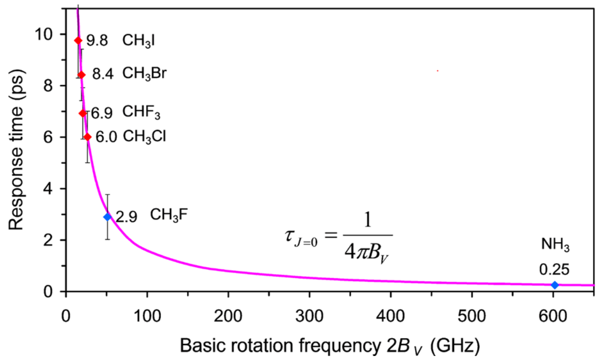


**Figure 4.** Molecular response time on the $J = 0 \rightarrow 1$ rotation transition of some symmetric top molecules as a function of the transition frequency $\nu_{J=0} = 2B_V$ (neglecting anharmonicities). The solid pink graph results from the uncertainty principle.

From the above analysis of the THz-TDS measurements and their interpretation in terms of MRT, we conclude that the THz-TDS experiments allow one to directly observe the fundamental time response of molecules to an external applied electric field in the presence of molecular collisions. This response is limited by the uncertainty principle and is determined by the inverse of the spitting frequency between adjacent levels, and thus, by the oscillation period on a transition. In this sense, it also determines the transition time to switch from one molecular state to another or to form a coherent superposition of states oscillating with the splitting frequency.

In classical terms, the response can also be explained as the onset and build-up time of a molecular oscillation and coherent emission of radiation, as this is observed as commensurate echoes[11−13] on the free induction decay.

In the frequency domain, MRT can be interpreted as a unification of the classical line shape theories of Lorentz and van Vleck−Weisskopf, allowing a continuous transition from a Lorentz to the van Vleck−Weisskopf shape and also integrating the limiting case of the Debye theory for dc fields. These fundamental theories could already be unified by explicitly introducing a molecular response time. The new analysis and interpretation of our data now shows that it is no longer necessary to experimentally derive this response for the different molecules, but to replace the response on a single transition by the inverse of the transition angular frequency.

## 5. CONCLUSION

In this contribution, we have investigated the time response of molecular transitions by observing the pulse reshaping of femtosecond THz-pulses which are propagating through polar vapors. From precise modeling of the pulse interaction with the molecular vapors, we could derive detailed insight into the time response of molecular transitions during and after an excitation. The measurements were performed on symmetric top molecules applying the powerful technique of THz time domain spectroscopy.[1−4,10] These measurements were analyzed directly in the time domain and parallel in the frequency domain by Fourier transforming the pulses and comparing the respective spectra with calculations based on the MRT.[2−4] The applied THz experimental setup allowed us to directly observe the ultimate time response of molecules to an external applied electric field in the presence of molecular collisions.

With a further refined response theory, we could show that the molecular response is obviously limited by the uncertainty principle and is determined by the inverse of the spitting frequency between adjacent levels of a transition and thus, defined by the oscillation period of a transition. In addition, this extended theory allows a natural unification of the basic collision and line-shape theories of Lorentz,[5] van Vleck−Weisskopf,[6] and Debye,[7] and it indicates that the previously introduced response time is naturally integrated in the line-shape theories as inverse frequency of an individual molecular transition. This no longer makes it necessary to experimentally determine the averaged response times of the different molecules.

## ■ AUTHOR INFORMATION

### Corresponding Author

*Phone: +4940 6700 623. Fax: +4940 6541 2640. E-mail: harde@hsu-hh.de.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We thank Bernhard Heinemann for his engaged development and improvement of the new THz-TDS system, which he could use to perform the measurements on some methyl halides and $CHF_3$.

## ■ REFERENCES

(1) Harde, H.; Katzenellenbogen, N.; Grischkowsky, D. Line-Shape Transition of Collision Broadened Lines. *Phys. Rev. Lett.* **1995**, *74*, 1307−1310.

(2) Harde, H.; Cheville, R. A.; Grischkowsky, D. THz Studies of Collision Broadened Rotational Lines. *J. Phys. Chem. A* **1997**, *101*, 3646−3660.

(3) Harde, H.; Cheville, R. A.; Grischkowsky, D. Collision Induced Tunneling in Methyl Halides. *J. Opt. Soc. Am. B* **1997**, *14*, 3282−3293.

(4) Harde, H.; Zhao, J.; Wolff, M.; Cheville, R. A.; Grischkowsky, D. THz Time-Domain Spectroscopy on Ammonia. *J. Phys. Chem. A* **2001**, *105*, 6038−6047.

(5) Lorentz, H. A. *Proc. Amst. Akad. Sci.* **1906**, *8*, 591−611.

(6) van Vleck, J. H.; Weisskopf, V. F. On the Shape of Collision Broadened Lines. *Rev. Mod. Phys.* **1945**, *17*, 227−236.

(7) Debye, P. *Polar Molecules*; Chemical Catalog Company: New York, 1929; Chapter V.

(8) Townes, C. H.; Schawlow, A. L. *Microwave Spectroscopy*; Dover Publications Inc.: New York, 1975.

(9) Heinemann, B.; Fox, C. J.; Harde, H. Improved Fast Scanning TeraHz Pulse System. *Ultrafast Phenomena XVI - Springer Series in Chemical Physics* **2009**, *92*, 684−686.

(10) Heinemann, B. *Weiterentwicklung und Einsatz eines Mess-Systems mit Asynchroner Abtastung zur Zeitaufgelösten Terahertz-Spektroskopie an Gasen*. Dissertation, Helmut-Schmidt-University, Hamburg, Germany, 2014.

(11) Harde, H.; Keiding, S.; Grischkowsky, D. THz Commensurate Echoes: Periodic Rephasing of Molecular Transitions in Free-Induction Decay. *Phys. Rev. Lett.* **1991**, *66*, 1834−1837.

(12) Harde, H.; Grischkowsky, D. Coherent Transients Excited by Subpicosecond Pulses of Terahertz Radiation. *J. Opt. Soc. Am. B* **1991**, *8*, 1642−1651.

(13) Harde, H.; Katzenellenbogen, N.; Grischkowsky, D. Terahertz Coherent Transients from Methyl Chloride Vapor. *J. Opt. Soc. Am. B* **1994**, *11*, 1018−1030.

(14) Landau, L. D.; Lifshitz, E. M. *Quantum Mechanics, Non-Relativistic Theory*; Pergamon Press Ltd: London, 1958.

DOI: 10.1021/acs.jpca.5b05909
*J. Phys. Chem. A* 2015, 119, 9085−9090