



Comment on ‘Rate coefficients for photoinitiated NO₂ unimolecular decomposition: energy dependence in the threshold regime’ [Chem. Phys. Lett. 358 (2002) 71]

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Abstract

Recently, Wittig and co-workers have published rate coefficients $k(E)$ for the unimolecular decomposition of photoinitiated NO₂ close to the dissociation threshold [Chem. Phys. Lett. 358 (2002) 71]. They found out that $k(E)$ for low angular momentum J exhibits a strong increase within 25 cm⁻¹ of the reaction threshold. The authors emphasize that their experimental results are surprising and cannot be understood quantitatively on the basis of current theory on NO₂. In this Comment we demonstrate that recent quantum mechanical calculations of NO₂ resonances on a global 3D-potential energy surface can indeed explain their data close to the dissociation threshold as well as for larger excess energies.

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The unimolecular dissociation reaction NO₂ → O + NO has played an important role in the understanding of unimolecular reactions and in the development of unimolecular rate theory (see [1] and references therein). Recently, Wittig and co-workers [2] have reported rate coefficients $k(E)$ for the photoinitiated unimolecular decomposition of NO₂ close to the dissociation threshold, which are an extension of earlier work [3]. They report that $k(E)$ for low J quantum number increases rapidly from 2×10^{10} to $\geq 1.3 \times 10^{11}$ s⁻¹ within 25 cm⁻¹

of the reaction threshold. In earlier measurements they covered the excess energy range 50–1000 cm⁻¹ [4]. A strong dependence of the average rate at threshold has also been documented for other molecules than NO₂, e.g., HONO [5]. The authors emphasize, however, that their findings cannot be understood quantitatively on the basis of the published theory on NO₂ and that the data are a strong challenge for high level theory in the future [2]. First we want to emphasize that the discussed measurements of the Wittig group are very nice and that they certainly represent the current state-of-the-art in the field. However, we do not quite agree with the interpretation of the data. In the current short contribution we want to demonstrate

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that recent quantum mechanical calculations of resonances on a global 3D-potential energy surface [6] can explain the data close to E_0 as well as for larger excess energies above the dissociation threshold quantitatively. Moreover, without any fitting parameter the wave packet calculations reproduce all data from the Wittig group and others within a factor of two between 0 and 1000 cm^{-1} of excess energy.

Our analysis is based upon quantum mechanical wave packet calculations on a global 3D potential energy surface (CASPT2) for NO_2 which was published very recently [6]. The dissociation dynamics was calculated on the lowest adiabatic PES of NO_2 . We have discussed this approximation in detail recently and details of the calculation as well as the features of the PES are described in [6]. The imaginary parts, $\Gamma/2$, of the calculated resonance energies are converted into state-specific dissociation rates according to

$$k_{\text{qm}}(E) = \frac{\Gamma}{\hbar}. \quad (1)$$

The resonances in the excess energy region 0–1500 cm^{-1} found for NO_2 above its threshold value of $E_0 = 25128.5 \text{ cm}^{-1}$ are displayed in Fig. 1. It is obvious that the calculated rates fluctuate

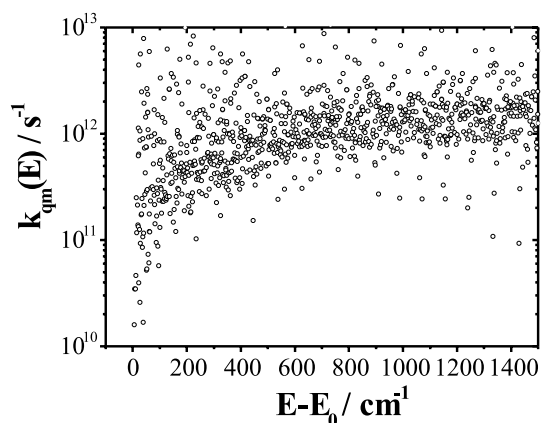


Fig. 1. State-resolved calculated dissociation rates ($J = 0$) for the reaction $\text{NO}_2 \rightarrow \text{NO} + \text{O}$ as a function of excess energy as obtained from the resonance poles [6]. Resonance energies and widths of NO_2 for total angular momentum $J = 0$ were studied by calculating the time evolution of a wave packet $\Phi(t)$. Resonance widths Γ are converted to specific rate constants $k_{\text{qm}}(E)$ via Eq. (1). For details see [6].

strongly around an average value. Close to the threshold, k_{qm} spans more than 2 orders of magnitude, however, with increasing energy the variations of k_{qm} in a given energy window are still at least one order of magnitude. Fluctuating dissociation rates for several small molecules have been observed in recent years [5] and have been found in several quantum mechanical studies [6], such that their existence is well established. Nevertheless, in view of the relatively large density of states at threshold and the nearly chaotic classical dynamics already far below the dissociation threshold the degree of fluctuations for NO_2 came as a surprise.

The degree of fluctuations that is observable in the experiment depends upon the frequency and the time resolution of the experiment. In high resolution double resonance experiments the full structure of resonances that partially already overlap in the threshold region is visible [7,8]. In time resolved experiments (with picosecond or femtosecond time resolution) the structure is already smoothed out by the larger bandwidths of the employed laser pulses [1,3,4,9–11]. In their recent study Wittig and co-workers [2] found a good compromise between time (10 ps) and energy (3 cm^{-1}) resolution. However, even in this experiment the laser usually excited more than one resonance and therefore the time resolved traces represent averages of several resonances. Moreover, due to the limited time resolution the broad resonances, which are present even at the threshold do not show up in the time resolved traces. Structure in the time resolved traces naturally appears when (broad) resonances tune in and out. This structure sensitively depends upon the energy and widths of the resonances. In [6] we have discussed the power and the limits in the absolute determination of the energies and widths of resonances for NO_2 . Nevertheless, we want to point out again at this point that the reproducible structure in the measured energy dependence of $k(E)$ is most likely due to the energy dependence of resonance structures and *not to the opening of individual channels* $W(E)$ in the classical expression for $k(E)$ from statistical theories

$$k(E) = \frac{W(E)}{h\rho(E)}. \quad (2)$$

In [6] we have shown that application of statistical theories may be a reasonable approximation for the description of the photo dissociation of NO_2 *on average*. Often $k(E)$ represents a reasonable average of the energy dependence of the individual quantum mechanical resonances. Problems arise, however, if the threshold energy region is considered. From Eq. (2) one would expect that a threshold rate exists that is equal to $[\hbar\rho(E)]^{-1}$ with $\rho(E)$ being the threshold density of states of the molecules. In the quantum mechanical picture the threshold rate is more difficult to define, since the resonances fluctuate strongly even at threshold. A pragmatic approach would be to consider the first resonance above threshold to be the threshold rate, but since in a experiment usually more than one resonance is excited this may also cause problems. The effect of the threshold rate upon the energy resolution can nicely be seen in the experiments from Wittig's group. In early experiments with picosecond time resolution the threshold rates were measured to be $1.6 \times 10^{11} \text{ s}^{-1}$, whereas the threshold rate determined in the most recent study was $2 \times 10^{10} \text{ s}^{-1}$, in good agreement with frequency domain measurements [7]. Obviously the larger bandwidth in the earlier experiment sampled more resonances directly above the dissociation threshold which resulted in a significantly higher threshold value [4]. The strong energy dependence of the measured $k(E)$ are easily explained by the rapid increase of the average resonance width. For the present case the resonances directly at threshold have a widths corresponding to a rate of $2 \times 10^{10} \text{ s}^{-1}$, however, very soon broader resonances tune in and decrease the average lifetime corresponding to a rate constant of about $1\text{--}2 \times 10^{11} \text{ s}^{-1}$.

In order to show the good agreement between the discussed experiments and theory we use the published resonance widths and energies and simulate experiments with different laser pulse widths and excitation energies. The 'signal' as a function of the laser pulse bandwidth in a simulated experiment is

$$S = \sum_i A_i (1 - \exp(-k_i t)) \quad (3)$$

with

$$A_i = \int_{-\infty}^{+\infty} P(E)L_i(E) dE. \quad (4)$$

In Eq. (4) $P(E)$ represents the laser pulse bandwidth (taken from [2,4]), approximated as a Gaussian, and $L_i(E)$ is the resonance width function, represented as a Lorentzian. With this prescription we can generate signals for the different experimental sets of data from the Wittig group in [2,4]. The signal rise described by Eq. (3) is multi-exponential by definition. This property of the NO_2 decomposition which actually has been observed experimentally [4] can, however, easily be covered by noise and/or finite time resolution. Therefore, in accordance with the data analysis in [2,4] we, after convolution of Eq. (3) with the cross correlation of pump and probe pulses of the particular experiment, fitted the generated signal to a mono-exponential expression. The results of this analysis are displayed in Fig. 2 together with the experimental data. As can be seen, the agreement between theory and experiment is very good. In particular, the threshold value, the energy dependence as well as the rates at higher energies are nicely (i.e., largely quantitatively) reproduced *without adjustable parameters* or tweaking parameters! Also the effect of different threshold rates for different experiments is very obvious. The deviations between experiment and theory are in general not larger than a factor of two in the energy range between 0 and 1000 cm^{-1} . The largest deviations occur in the threshold region where the absolute positions and widths of the resonances matter most. A correct (quantitative) reproduction of the structure of the measured data in the threshold region should not be expected, because absolute widths and positions of resonance states sensitively depend upon subtle features of the PES in this region. However, the strong energy dependence is predicted *ab initio* without any further assumptions.

We want to point out here that when discussing threshold rates within the framework of statistical theories and Eq. (2) the density of states at the threshold is a crucial quantity. In the quantum mechanical approach this is not the case anymore. If the number or density of resonances are determined it may provide some guidance of how to

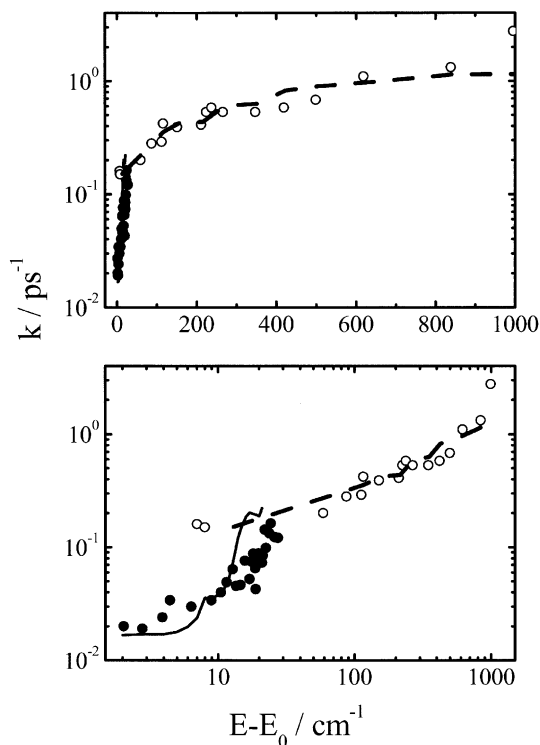


Fig. 2. Experimental rate constants for the unimolecular decomposition of NO_2 (●: measured with ~ 10 ps time resolution, from [2]; ○: with ~ 1 ps time resolution, from [4]) and comparison with model calculations based upon the calculated dissociation rates of Fig. 1, as described in the text (solid line: with 10 ps time resolution and a bandwidth of 3 cm^{-1} ; dashed line: with 1 ps time resolution and a bandwidth of $20\text{--}80 \text{ cm}^{-1}$). Upper panel: semi-logarithmic plot with linear energy scale for the excess energy region $0\text{--}1000 \text{ cm}^{-1}$; lower panel: same energy interval but double logarithmic plot for easier inspection of the low excess energy region. Note, that the highest threshold rate constants (filled circles) taken from [2] are actually lower bounds due to limited time resolution of the experiment.

count states in statistical approaches in the quasi continuum of states above the dissociation threshold, which is a non-trivial task [12]. In any case, in the quantum mechanical picture the results do hardly depend on the density and number of resonances. Wittig and co-workers suspect that the small $k(E)$ values when E is slightly in excess of E_0 may be due to long-range interactions that may play a role in the threshold regime, as discussed already in [3]. We agree that properties of the reacting molecule in the threshold region may be sensitive to the long-range

interfragment potential [12,13] and to the large number of (possibly interacting) PESs at large distances. Although, we cannot rule out a contribution of long-range interactions to the threshold rates, it looks as if they play only a minor role. Instead, in the quantum mechanical resonance picture, the observed energy dependence in the threshold region appears to be largely a natural consequence of the resonance structure close to the threshold, and the same holds for the high excess energy region. Also structure (steps) in the energy dependence of the rate constants can be easily understood – without extra assumptions – when resonance widths as a function of energy are analyzed quantitatively.

In summary, NO_2 has always been appreciated by experimentalists as well as theoreticians as a benchmark system. Its dynamics, quantum yields, and spectroscopy, nevertheless, has puzzled and intrigued generations of researchers. Due to recent advances and achievements in both experiment and ab initio theory many of the mysterious data of NO_2 can now be explained. In particular, we believe that the specific rate constants of NO_2 close to the dissociation threshold – which have been the subject of a long standing debate – can now be rationalized within the concept of quantum mechanical resonances. It can indeed be calculated ab initio with good accuracy – in good agreement with experimental data [1–4,6–11].

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