Supporting Information
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Probing the Barrier for Internal Rotation of the Retinal Chromophore**
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Supplementary information A—validity of the calorimetric approach

Let $G(\varepsilon; T)$ denote the internal energy distribution of ions which are equilibrated to a canonical temperature $T$. Let $k(\varepsilon)$ denote the microcanonical rate constant for fragmentation i.e. if all ions had energy $\varepsilon$, their decay would be given by $I(t) = k(\varepsilon)e^{-k(\varepsilon)t}$. The measured signal is then given by an integration over the energy distribution which is shifted by the photon energy, $\varepsilon_{ph}$:

$$I(t) = \int_0^\infty G(\varepsilon; T)k(\varepsilon + \varepsilon_{ph})e^{-k(\varepsilon+\varepsilon_{ph})t}d\varepsilon \equiv \int_0^\infty G(\varepsilon; T)r(\varepsilon + \varepsilon_{ph})d\varepsilon \equiv <r(\varepsilon + \varepsilon_{ph})>_T.$$

It is worth noting that the decay is intrinsically multi-exponential. A summation over all distinct energy levels is replaced here by the integral over thermal energies due to the high density of vibrational states in the RPSB molecule ($\approx 10^{13}$ per 1 cm$^{-1}$ at $\varepsilon = 0.3$ eV). We use the definition of $r(\varepsilon) = k(\varepsilon)e^{-\kappa(\varepsilon)t}$ to simplify the notation and to emphasize that the following derivation is valid also for different kinds of calorimetric probes (not only delayed fragmentation) in which $r(\varepsilon)$ may have a different form.

Thus the signal one measures is a thermal average of the function $r(\varepsilon + \varepsilon_{ph})$. Provided that $G(\varepsilon; T)$ is significant only for $\varepsilon \ll \varepsilon_{ph}$, one can use a Taylor expansion with $\varepsilon$ as a small variable:

$$<r(\varepsilon + \varepsilon_{ph})>_T \approx <r(\varepsilon_{ph}) + \left(\frac{\partial r}{\partial \varepsilon}\right)_{\varepsilon_{ph}} \varepsilon + \frac{1}{2} \left(\frac{\partial^2 r}{\partial \varepsilon^2}\right)_{\varepsilon_{ph}} \varepsilon^2 + ...>_T =$$

$$= r(\varepsilon_{ph}) + \left(\frac{\partial r}{\partial \varepsilon}\right)_{\varepsilon_{ph}} \varepsilon + \frac{1}{2} \left(\frac{\partial^2 r}{\partial \varepsilon^2}\right)_{\varepsilon_{ph}} \varepsilon^2 <\varepsilon>_T + ...$$

Noting that the average energy is given by: $U(T) = <\varepsilon>_T$, and using the relation:

$$<\varepsilon>_T = U(T)^2 + \sigma(T)^2,$$

where $\sigma(T)^2 = <(\varepsilon - U)^2>$ is the variance of the the energy distribution, we arrive at the expansion:

$$<r(\varepsilon + \varepsilon_{ph})>_T \approx <r(\varepsilon_{ph}) + \left(\frac{\partial r}{\partial \varepsilon}\right)_{\varepsilon_{ph}} U(T) + \frac{1}{2} \left(\frac{\partial^2 r}{\partial \varepsilon^2}\right)_{\varepsilon_{ph}} (U(T)^2 + \sigma(T)^2)>_T + ...$$

In the ion calorimetric approach the goal is to correlate the signal measured at a specific thermal energy $T_1$, excited by a photon of energy $\varepsilon_{ph}$, to that measured with a different temperature $T_2$ and photon of energy $\varepsilon_{ph}' = \varepsilon_{ph} - \Delta \varepsilon_{ph}$. Thus one requires that

$$<r(\varepsilon + \varepsilon_{ph}')>_T(1) = <r(\varepsilon + \varepsilon_{ph}' - \Delta \varepsilon_{ph})>_T(2)$$

$$= r(\varepsilon_{ph}') + \left(\frac{\partial r}{\partial \varepsilon}\right)_{\varepsilon_{ph}'} U(T_2) - \Delta \varepsilon_{ph} + \frac{1}{2} \left(\frac{\partial^2 r}{\partial \varepsilon^2}\right)_{\varepsilon_{ph}'} (U(T_2)^2 + \sigma(T_2)^2 - 2U(T_2)\Delta \varepsilon_{ph} + \Delta \varepsilon_{ph}^2) + ...$$

Where $\varepsilon - \Delta \varepsilon_{ph}$ was the small expansion parameter for the right hand side of the equation. Comparing the first order terms (marked in blue in the above equation) leads to the condition:

$$U(T_1) = U(T_2) - \Delta \varepsilon_{ph}.$$ 

Thus, a correlation between the two measurements occurs when the photon energy is equal to the change in average energy resulting from the change in temperature. The second order terms in the expansion (marked in green in the equation above) requires, in addition that:

$$\sigma_{T_2}^2 \approx \sigma_{T_1}^2$$

The change in temperature should hence not significantly change the width of the energy distribution, which can be satisfied by using small steps in temperature. Higher order terms in the Taylor expansion lead to further requirements for the higher statistical moments of the energy distribution. Since the canonical distribution at room temperature can be well approximated by a Gaussian, statistical moments of orders higher than three are negligible. The canonical distribution is slightly skewed and thus has a third order statistical moment, but the change in asymmetry upon temperature can be shown to be negligible.

The main conclusions of the following derivation are:

- The ion calorimetric approach measures the change in average energy as a function of temperature.
- The energy of the probe photon has to be much larger than the ion’s thermal energy, thus “high” temperatures cannot be probed by “low”-energy photons.
- It is important to choose small temperature steps, such that the change in the width of the energy distribution is small.
In the following a brief intuitive explanation will be given for the heat capacity of a single hindered rotator, shown in Figs. 6 and S1.

At low temperatures, the dynamics of a hindered rotator is similar to that of a harmonic oscillator, in that it oscillates around the angle corresponding to the minimum energy, a motion that is called `libration`. The heat capacity of a quantum harmonic oscillator starts at \( 0 \) and rises monotonously towards the high temperature asymptotic limit of \( \frac{1}{2} k_B \). Since the frequencies of libration are very small (in the range of 20-25 cm\(^{-1}\) for the RPSB), the characteristic temperature where the high temperature limit is approached, \( T_{\text{HO}} \), is very small. For the RPSB \( T_{\text{HO}} \) is well below 100K. Note that this initial rise in the heat capacity is a quantum effect; therefore it is not seen in classically calculated heat capacity curves. For classical calculations, shown by the dashed lines in Fig. 6, the low temperature limit of the heat capacity is \( 1k_B \).

On the other hand, for very high temperatures, the dynamics of a hindered rotator is similar to that of a free internal rotator, the heat capacity of which is only \( \frac{1}{2} k_B \). Thus one expects that at temperatures above \( T_{\text{FR}} = \frac{\Delta E_0}{k_B} \) (where \( \Delta E_0 \) is the barrier height for internal rotations) the heat capacity of the hindered rotator will decrease towards the \( \frac{1}{2} k_B \) limit. For the RPSB, as an example, the barrier height is calculated to be 1059 cm\(^{-1}\), correspondingly.

In the transition region, \( T_{\text{HO}} < T < T_{\text{FR}} \), corresponding to energies below but close to the barrier energy for internal rotations, the anharmonicity of the potential energy surface results in an increase in the density of states (clearly seen in Fig. 5 for energies above 700 cm\(^{-1}\)). Correspondingly, the heat capacity initially rises to values above \( 1k_B \), before starting to decrease towards the \( \frac{1}{2} k_B \) limit. It is therefore expected that the heat capacity reaches a maximum at an intermediate temperature, \( T_m \), and that the position of this maximum is correlated with the barrier energy for internal rotation.

\[ C_{\text{HO}} / k_B \]

\[ T_{\text{HO}} < T < T_{\text{FR}} \]

\[ C_{\text{FR}} / k_B \]

\[ T_{\text{FR}} \]

\[ T_m \]

Figure S1. Heat capacity of a hindered rotator.
Supplementary information C– Examples of the power law fits to the data

**Figure S2.** Yield of neutral hits on the MCP detector as a function of time after excitation by a laser with wavelength \( \lambda = 500 \text{ nm} \). Prior to acceleration the ions were thermalized in the RF trap to a temperature of 173K.

**Figure S3.** Yield of neutral hits on the MCP detector as a function of time after excitation by a laser with wavelength \( \lambda = 530 \text{ nm} \). Prior to acceleration the ions were thermalized in the RF trap to a temperature of 197K.
To demonstrate that it is indeed possible to determine the heat capacity properties associated with one degree of freedom by comparing the total heat capacity of two closely related molecules, we have calculated the heat capacity of a derivative of the RPSB, in which a Methyl group was moved from the C-9 carbon to the C-8 carbon. Consequently the interaction between this Methyl group and the one on the β-ionone ring increases significantly the barrier for internal rotation of the ring. The advantage of this model is that the total number of atoms is the same and thus the harmonic contributions to the heat capacity should be the same. Denoting this derivative as ‘R2’, we define a differential heat capacity as the difference $C_D = C_{RPSB}(T) - C_{R2}(T)$, between the heat capacity of the entire RPSB and of this derivative. Figure S4 shows the calculation, which resembles in shape and in the location of $T_m$ the calculated heat capacity of the single degree corresponding to the rotation of the β-ionone ring.

**Figure S4.** Bottom: Differential heat capacity defined as the difference in heat capacity between the RPSB shown as the top diagram in the figure, and the heat capacity of the R2 derivative. Top: the heat capacity associated with the single degree of freedom corresponding to the hindered rotation of the β-ionone ring in the RPSB.