Supplemental Material for B707833C:

"*In situ* optical monitoring of RDX nanoparticles formation during rapid expansion of supercritical CO_2 solutions", by Takuya Matsunaga,[a] Andrei V. Chernyshev,[b] Evgeni N. Chesnokov,[b] and Lev N. Krasnoperov[a]

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Appendix A. Calibration of the sensitivity of the ICCD camera

Two independent techniques were used for the sensitivity calibration: Rayleigh scattering from air and Mie scattering from standard spherical polystyrene latex particles.

A.1. Calibration based on Rayleigh scattering from air

The laser beam was focused by a spherical lens (focal length 200 mm at 248 nm), so that the focal point was in the field of view of the optical system composed of the imaging optics (a single lens or a doublet) and the camera. The calibration then consisted of the accumulation of a number of pulses in a single frame, measuring the total laser energy, and processing of the beam image formed by Rayleigh scattering. The number of scattered photons was evaluated theoretically.

The Cartesian coordinates used below: x axis is parallel to the direction of the incident laser beam, y axis is along the direction from the sampling zone to the camera, and z axis is along the jet and perpendicular to the x and y directions. The optical system magnification was measured using thin wire as a scattering object and a translation stage to shift the wire by known distances. The magnification of the system was 5.1 ± 0.1.

When using Rayleigh scattering from air, the sensitivity was determined as:

$$\beta = \frac{N_{ICCD,Rayleigh}}{N_{sc,Rayleigh}} \qquad \text{(A1)}$$

where $N_{ICCD,Rayleigh}$ is the total number of counts per unit length along the X axis per pulse, and $N_{sc,Rayleigh}$ is the corresponding total number of scattered photons from unit length that hit the photocathode of the camera per pulse. Integrating the curve in Fig. 5(b) in the Z-direction, the total number of counts per length of one pixel of the ICCD camera, $\tilde{N}_{ICCD,Rayleigh}$, is obtained. Then the $N_{ICCD,Rayleigh}$ is calculated using the magnification of the optical system as:

$$N_{ICCD,Rayleigh} = \tilde{N}_{ICCD,Rayleigh} \frac{M}{L} \qquad \text{(A2)}$$

where M is the magnification and L is the size of one pixel in the ICCD camera in the X-direction. $N_{sc,Rayleigh}$ is calculated as:

$$N_{sc,Rayleigh} = nN_{inc} \left(\frac{d\sigma}{d\Omega} \right)_{molecule} \Omega \qquad \text{(A3)}$$

where N_{inc} is the number of incident photons per pulse, n is the number density of molecules, σ is the Rayleigh scattering cross section, Ω is the solid angle for the light collection, and $\left(\frac{d\sigma}{d\Omega} \right)_{molecule}$ is the differential scattering cross section of a molecule for unpolarized incident light at the observation angle of 90°. N_{inc} is given by

$$N_{inc} = \frac{E_{inc}\lambda}{hc} \qquad \text{(A4)}$$

where h is the Planck constant, c is the speed of light, E_{inc} is the energy of the incident laser light per pulse, and λ is the wavelength of the incident laser light.
From equations A1 - A4, the sensitivity is calculated as follows:

$$\beta = \frac{hc\tilde{N}_{ICCD,Rayleigh}}{nE_{inc}\lambda\left(\frac{d\sigma}{d\Omega}\right)_{molecule}\Omega}\frac{M}{L}. \tag{A5}$$

The sensitivity of the camera determined in this way was 5.2 ± 0.2 counts per incident photon.

A.2. Calibration based on Mie scattering from the standard latex particles

In these experiments, laser light was not focused, but instead a uniform rectangular beam was formed using a rectangular orifice (0.9 mm × 1.3 mm). Standard latex particles with the diameter of 102 and 152 nm obtained from Duke Scientific Corporation were used. The sensitivity determined based on Mie scattering was done in the same manner as using Rayleigh scattering from air. The total number of counts per standard latex particle $N_{ICCD,latex}$ is obtained from the scattering images. Using the differential scattering cross section calculated using Mie theory, the total number of scattered photons from a single latex particle is

$$N_{sc,latex} = \frac{N_{inc}}{A}\left(\frac{d\sigma}{d\Omega}\right)_{particle}\Omega \tag{A6}$$

where A is the cross sectional area of the incident laser beam. The cross sectional area was defined by the rectangular slit. The differential scattering cross section was calculated using the Fortran program, Chiral.[1] The index of refraction of 1.803+0.0072i (see Appendix B) for polystyrene was used for the calculation. The sensitivity is then calculated as:

$$\beta = \frac{hcAN_{ICCD,latex}}{E_{inc}\lambda\left(\frac{d\sigma}{d\Omega}\right)_{particle}\Omega}. \tag{A7}$$

The sensitivities determined based on Mie scattering from the latex particles of 102 nm was 5.1 ± 0.6 counts per photon and from 152 nm was 5.3 ± 0.6 counts per photon. The average value is 5.2 ± 0.6 counts per photon.

Appendix B. Evaluation of the index of refraction of polystyrene and RDX at 248 nm

B.1. Polystyrene

The complex index of refraction m for a non-magnetic material is given by

$$m = n + ki = \sqrt{\varepsilon_r} \tag{B1}$$

where ε_r is the relative complex dielectric constant of the material, and n and k are the real and the imaginary parts of the index of refraction, respectively. The complex dielectric constant of polystyrene at 248 nm wavelength is $\varepsilon_r(248nm) = 3.251 + 0.260i$ as obtained from the literature data.[2] From equation B1, n and k are 1.803 and 0.0072, respectively.

B.2. RDX

Little information is available for the evaluation of the index of refraction of RDX at the desired wavelength. In this paper the experimentally obtained reflection spectrum of RDX measured over the wavelength range from 185 nm to 525 nm by Marinkas *et al.*,[3] was used as the basis for the index of refraction determination. The spectrum was fitted with the theoretical curve based on the Lorentz model with several oscillators.[4]

Using equation B1, the real and the imaginary indices of refraction are written as:

$$n = \sqrt{\frac{1}{2}\left(\varepsilon_r' + \sqrt{\varepsilon_r'^2 + \varepsilon_r''^2}\right)} \tag{B2}$$

and

$$k = \frac{\varepsilon_r''}{2n}, \tag{B3}$$

where ε_r' and ε_r'' are the real and imaginary parts of the dielectric constant, respectively. According to the Lorentz model with several oscillators, the complex dielectric constant is expressed as

$$\varepsilon_r(\omega) = 1 - \sum_{j=1}^{N} \frac{f_j \omega_p{}^2}{\left(\omega^2 - \omega_j{}^2\right) + i\omega\gamma_j} \tag{B4}$$

where N is the number of oscillators, f_j is the oscillator strength, ω_p is the plasma frequency, ω_j is the oscillator frequency (resonance frequency), and γ_j is the damping constant. In our calculations, we used three oscillators ($N = 3$) to fit the experimental data from Ref. 26. Modifying equation B4, the real and imaginary parts of the dielectric constant are:

$$\varepsilon_r'(\omega) = 1 - \sum_{j=1}^{N} \frac{f_j \omega_p{}^2\left(\omega^2 - \omega_j{}^2\right)}{\left(\omega^2 - \omega_j{}^2\right)^2 + \omega^2\gamma_j{}^2} \tag{B5}$$

and

$$\varepsilon_r''(\omega) = \sum_{j=1}^{N} \frac{f_j \omega_p{}^2 \omega\gamma_j}{\left(\omega^2 - \omega_j{}^2\right)^2 + \omega^2\gamma_j{}^2}. \tag{B6}$$

Using the real and the imaginary indices of refraction, the reflectance of the material R is given by

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \tag{B7}$$

for normal incident light. From equations B2, B3 and B5-B7, R is expressed as a function of frequency ω. The experimental RDX reflection curve[3] was fitted using $f_j \omega_p{}^2$, ω_j, and γ_j as fitting parameters, and ω as an independent variable. The optimum values of parameters are: $f_1 \omega_p{}^2 = 2.05 \times 10^{-3} nm^{-2}$, $\omega_1 = 2.29 \times 10^{-2} nm^{-1}$, $f_2 \omega_p{}^2 = 8.26 \times 10^{-6} nm^{-2}$, $\omega_2 = 4.87 \times 10^{-3} nm^{-1}$, $\gamma_2 = 1.22 \times 10^{-3}$, $f_3 \omega_p{}^2 = 5.11 \times 10^{-6} nm^{-2}$, $\omega_3 = 3.95 \times 10^{-3} nm^{-1}$, and $\gamma_3 = 7.28$. Using these values, the complex index of refraction of RDX at the wavelength 248 nm was calculated as $m = 1.678 + 0.645i$.

Appendix C. The dilution by air entrainment estimated based on the temperature profile

In the derivation below, it was assumed that the entrained air has ambient temperature (298 K), and, as estimates show that the heat exchange by conduction can be neglected. The molar enthalpy of the mixture H_{mix} at the vertical point z along the jet is given by

$$H_{mix}(T(z)) = x_{CO_2} H_{CO_2}(T(z)) + x_{air} H_{air}(T(z)) \qquad \text{(C1)}$$

where $T(z)$ is the temperatures of the jet, H_{CO_2} and H_{air} are the molar enthalpy of CO_2 and air, respectively, and x_{CO_2} and x_{air} are the mole fractions of CO_2 and air in the jet, respectively. The molar enthalpy of the mixture is also written as

$$H_{mix}(T(z)) = x_{CO_2} H_{CO_2}(T_i) + x_{air} H_{air}(T_0) \qquad \text{(C2)}$$

where T_i, and T_0 are the initial temperature of the jet and the temperature of surrounding air. The molar enthalpies of CO_2 and air are obtained by integration of the molar heat capacities c_{p,CO_2} and $c_{p,air}$ as follows:

$$\begin{aligned} H_{CO_2} &= \int c_{p,CO_2} dT \\ H_{air} &= \int c_{p,air} dT \end{aligned} \tag{C3}$$

The molar heat capacity of CO_2 is larger than that of air due to the vibrational contribution of the doubly degenerate O-C-O bending mode at 667 cm^{-1}, c_{vib} given as

$$c_{vib} = 2R\left(\frac{h\nu}{kT}\right)^2 \frac{\exp(h\nu/kT)}{(\exp(h\nu/kT)-1)^2} \tag{C4}$$

where R is the gas constant, h is Plank's constant, ν is the vibrational frequency (in this case 667 cm^{-1}), and k is Boltzmann constant. Fortuitously, equation C4 gives a very good linear dependence of the heat capacity on temperature over the temperature range between 250 K and 300 K:

$$c_{vib} = (-4.65 + 0.0408\ T)\ \mathrm{J\ mol^{-1}K^{-1}} \tag{C5}$$

Assuming that the heat capacity of air over this temperature range is constant, the mole fraction of CO_2 is

$$x_{CO_2} = \frac{T_0 - T(z)}{T_0 - T_i - 0.160(T - T_i) + 1.40\times10^{-3}\left(T^2 - T_i^2\right)} \tag{C6}$$

Equation C6 was used to estimate the jet dilution caused by the air entrainment based on the temperature profile $T(z)$.

References

1 T. Wriedt, *http://www.iwt-bremen.de/vt/laser/wriedt/index_ns.html*.

2 T. Inagaki, E. T. Arakawa, R. N. Hamm and M. W. Williams, *Physical Review B*, 1977, **15**, 3243-3253.

3 P. L. Marinkas, J. E. Mapes, D. S. Downs, P. J. Kemmey and A. C. Forsyth, *Molecular Crystals and Liquid Crystals*, 1976, **35**, 15-25.

4 A. B. Djurišić and B. V. Stanić, *Applied Optics*, 1998, **37**, 2696-2698.