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Systematics of Collision-Induced Light Emission from Hot Matter[†]

A. Gross,[‡] Mikael Kjellberg,[§] and R. D. Levine*[,‡,||]

The Fritz Haber Research Center for Molecular Dynamics, The Hebrew University of Jerusalem, Jerusalem 91904, Israel, Department of Experimental Physics, Gothenburg University and Chalmers University of Technology, SE-41296 Gothenburg, Sweden, and Department of Chemistry and Biochemistry, The University of California at Los Angeles, Los Angeles, California 90095

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The hypersonic impact of a molecular cluster at a hard surface generates a hot and compressed globule that in a very short while expands and shatters. Even at impact velocities below the onset of ionization this hot matter has a time varying transient dipole that can emit light. We discuss the spectral range and the power (in absolute units) of the emission spectrum. The computational results for the emission spectrum from our molecular dynamics simulation are compared to extrapolations of experimental results for collision-induced absorption at lower energies. The very short time interval during which the cluster survives intact means that the emitted power is low so options for increasing the yield of photons are discussed.

Introduction

Collision-induced (light) absorption, CIA, in mixtures of rare gases at ordinary temperatures is well-studied and understood.[1−8] The absorption is due to a transient dipole moment that is created due to the distortion of the spherical charge distributions of two dissimilar colliding atoms. The duration of change in dipole moment scales as the duration of the binary collision, τ_c. On the basis of the uncertainty principle the width, in frequency, of the absorption spectrum scales as $1/\tau_c \approx v/a$, where v is the collision velocity and a the range of the interatomic force.[9] Thus, collisions in room temperature are familiar as absorption in the far-IR. But if the collision is at supersonic velocity we expect the spectrum to shift to the near-IR and even into the visible range. For us, the motivation for working at higher frequencies is that such spectra probe the extreme conditions created within impact heated clusters.[9−18] The practical advantage is that detectors in the shorter wavelength regime are significantly more efficient. There is also another way whereby the collision-induced spectrum can occur at higher frequencies and this is to collisionally perturb a homonuclear diatomic molecule. Such a molecule will not be IR active in the low-density limit but will exhibit a pressure-dependent spectrum whose vibrational part extends to the near-IR[19]

Two comments about impact-heated clusters are relevant to our work. One is that the (observed[17]) onset of ionization of the cluster is a very steep function of the impact velocity with an effective threshold that is of the order of 10 km/s for ordinary molecules and higher for rare gases. Therefore, up to fairly high energies of impact it is justified to use classical molecular dynamics simulations. The other point is that despite the high density within the compressed cluster it is realistic to describe it in terms of binary collisions.[11] The reason is that typically only pairs of atoms (for a rare gas cluster, or pairs of molecules otherwise) are strongly interacting. What this means for the dipole moment of the entire cluster is that it is well-approximated by the dipole moments of individual collisions. This approximation is not essential for computing the dipole and the spectrum but it is very useful in interpreting the results of the computations.

Current progress in the study of collision-induced (light) absorption is much concerned with obtaining accurate (and not only realistic) dipoles as functions of the interatomic distance(s).[20−22] For collisions at such high velocities where the atoms get quite close to one another and significant promotion of electrons into higher orbitals[23] is likely, we do not even have fully reliable realistic dipole functions. Therefore we proceed in two complementary ways. One is to compute the spectrum by using the currently available input and the other is to extrapolate experimental results for the collision-induced spectrum to the extreme conditions that prevail in (supersonic) impact-heated clusters. Such an extrapolation requires extending the range of the relevant dimensionless variables by 2 orders of magnitude. On its own this is a rather questionable procedure but it is motivated by the long-recognized observation[2,5,7,24,25] that the collision-induced spectrum is characterized by two moments with a third moment that is small because it is a quantal correction. We computed these moments at both ordinary and extreme conditions and showed that they scale appropriately.[26] Therefore we are confident that the spectrum itself can be suitably scaled.

We look for systematics because we expect that observing light emission is not going to be easy. The simple physical argument is clear. The ν^3 scaling of spontaneous emission means that the lifetime for emission in the near-IR is going to be of the order of 10^{-7} s or more. The duration of the atom−atom collision at higher velocities is less than 10^{-13} s so the probability of photon emission during a collision is below 10^{-6}. To overcome such low odds of emission per collision we need lots of collisions per cluster, as high a dipole moment as possible, extending the emission frequencies as much toward the visible as possible, etc. It has not escaped our attention that the ultimate solution is to disengage the two time scales. We

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* Address correspondence to this author. Fax: 972-2-6513742. E-mail: rafi@fh.huji.ac.il.

[‡] The Hebrew University of Jerusalem.

[§] Gothenburg University and Chalmers University of Technology.

[||] The University of California at Los Angeles.

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want the emission to be collision induced but we also want the emission not to be limited to the duration of the collision.

Spectral Sum Rules

We consider an atom−atom collision so that there is just one nuclear coordinate. The dipole moment function $\mu(\mathbf{R})$ is defined as the expectation value of the electronic dipole moment $\mathbf{r}$ in the electronic state $|e\rangle$,

$$\mu(\mathbf{R}) = \mu(R)\,\hat{\mathbf{R}} = e\langle e|\mathbf{r}|e\rangle \tag{1}$$

where $\hat{\mathbf{R}}$ is the unit vector in the direction of the internuclear distance $\mathbf{R}$ and e is the charge of the electron. The time dependence of the dipole moment function, which is required for computing the spectrum, is obtained from a molecular dynamics simulation of the cluster impact. The (semiclassical) spectrum is determined by $|\mu(\nu)|^2$ where $\mu(\nu)$ is the frequency Fourier transform of $\mu(R(t))$

$$\mu(\omega) = \int \mathrm{d}t\, e^{i\omega t} \boldsymbol{\mu}(R(t)) \tag{2}$$

As usual, the frequency (in s^{-1}) is related to the frequency ν expressed in wavenumbers by $\omega = 2\pi c\boldsymbol{\nu}$. The spectral moments are moments of $|\mu(\nu)|^2$. Because the classical trajectory $R(t)$ is an even function of time (in the range $-\infty < t < \infty$), $|\mu(\nu)|^2$ is an even function of the frequency (in the range $-\infty < \nu < \infty$) and all its odd moments vanish identically. In particular, the first classical sum, S_1,

$$S_1 = \int \nu|\mu(\nu)|^2\, \mathrm{d}\nu \tag{3}$$

vanishes. Quantum mechanically the odd moments need not vanish. For example, the first spectral moment equals, up to universal constants, the sum of the oscillator strengths, $f_{vv'}$, for transitions on the ground electronic state $|e\rangle$ from an initial state $|v\rangle$ to all final states $|v'\rangle$ of the relative motion

$$\begin{aligned}\sum_{v'} f_{vv'} &= \sum_{v'} \frac{2m_e(E_{v'} - E_v)}{\hbar^2}|\langle v|e\langle e|\mathbf{r}|e\rangle|v'\rangle|^2 \\ &= \sum_{v'} \frac{2m_e(E_{v'} - E_v)}{\hbar^2}|\langle v|\mu(R)|v'\rangle|^2\end{aligned} \tag{4}$$

m_e is the mass of the electron. In the Born−Oppenheimer approximation the states $|v\rangle$ of the relative motion are eigenfunctions of the potential $V(R)$ so that E_v is the eigenvalue of the Hamiltonian of the relative motion in the state $|v\rangle$.

The explicit summation over a complete set of final states results in

$$\sum_{v'} f_{vv'} = \frac{m_e}{\hbar^2}\langle v|[\mu(\mathbf{R}),[K_N,\mu(\mathbf{R})]]|v\rangle \tag{5}$$

K_N being the nuclear kinetic energy. By evaluating the double commutator we find the first sum rule for vibrational transition on a sole electronic state, in our case the ground state, to be

$$\sum_{v'} f_{vv'} = \frac{m_e}{M}\left\langle v\left|\left(\frac{\mathrm{d}\mu(\mathbf{R})}{\mathrm{d}\mathbf{R}}\right)^2\right|v\right\rangle \tag{6}$$

M is the nuclear reduced mass. The value of the zero moment of the oscillator strength, the first sum rule, is outright positive as it is an expectation value of a positive operator. Thus the sum is finite and not zero.

The classical sum S_1 (eq 3) vanishes because of symmetry. Since the analytical evaluation of the sum with use of quantum mechanics (eq 6) is finite we must conclude that the classical spectrum is not symmetric. Physically the spectrum arises because the dipole is varying with time and examination shows that the rate of change of the dipole is not the same in the two mechanics. Taking for simplicity a head-on collision, the classical time derivative of the dipole, denoted by a dot, is $\dot{\mu}(t) = \mu'(R(t))\dot{R}(t)$, while treating the dipole moment as a quantum operator on the nuclear states reveals a second contribution, a quantum correction[27]

$$\frac{\mathrm{d}\mu(R)}{\mathrm{d}t} = (i\hbar)^{-1}[\mu(R),K_N] = \mu'(R)\frac{P_R}{M} - i\hbar\frac{\mu''(R)}{2\,M} \tag{7}$$

Here P_R is the momentum for the relative motion and the dash is a derivative with respect R. Our semiclassical approach uses the quantal time derivative of the dipole, eq 7, followed by replacing the operators by functions evaluated along a classical trajectory and finally Fourier transforming the result into the frequency space. The classical limit of P_R/M is $\dot{R}(t)$ so the first term in (7) agrees with the purely classical result. According to the derivative theorem for Fourier transform (FT) if $\mu(\nu)$ is the FT of $\mu(t)$, which we write as $\mu(t) \leftrightarrow \mu(\nu)$, then the FT of $\dot{\mu}(t)$ is $2\pi i\nu\mu(\nu)$, where $\dot{\mu}(t)$ is the time derivative of the dipole, $\dot{\mu}(t) \leftrightarrow 2\pi i\nu\mu(\nu)$. Accordingly, the Fourier transform of the quantal dipole velocity, eq 7, is

$$\mu'(R(t))\frac{\mathrm{d}R(t)}{\mathrm{d}t} - i\hbar\frac{\mu''(R(t))}{2M} \leftrightarrow i(2\pi\nu\mu(\nu) - \hbar\zeta(\nu)) \tag{8}$$

Here $\zeta(\nu)$ is the FT of $\mu''(R(t))$ and as such it is a symmetric function of the frequency as $\mu''(R(t))$ is a symmetric function of time. In the semiclassical limit the magnitude of the quantum correction $\zeta(\nu)$ is computed from the classically determined time dependence of the interatomic distance $R(t)$.

The dipole function is a function of frequency such that the FT of the dipole velocity is given by eq 7 as

$$\epsilon(\nu) = (2\pi\nu\mu(\nu) - \hbar\zeta(\nu))/2\pi\nu \tag{9}$$

so that, due to the quantum correction in eq 7, the first sum does not vanish

$$\begin{aligned}S_1 &= \int (2\pi\nu)^{-1}(2\pi\nu\mu(\nu) - \hbar\zeta(\nu))^2\, \mathrm{d}\nu \\ &= -\hbar\int (2\mu(\nu)\,\zeta(\nu))\, \mathrm{d}\nu\end{aligned} \tag{10}$$

where both $\mu(\nu)$ and $\zeta(\nu)$ are symmetric with respect to the frequency. By including the quantum correction to the dipole velocity the first sum is finite and of the order of $\hbar$ and its explicit expression, eq 10, also agrees with the analytical sum in eq 6.

The first moment of the oscillator strength, which is the second moment of the spectrum,

$$\begin{aligned}\sum_{v'}(E_{v'} - E_v)f_{vv'} &= \frac{2m_e}{\hbar^2}\sum_{v'}(E_v - E_{v'})^2|\langle v|\mu(R)|v'\rangle|^2 \\ &= \frac{2m_e}{\hbar^2}\langle v|([H,\mu(R)])^2|v\rangle \\ &= 2m_e\left\langle v\left|\left(\frac{\mathrm{d}\mu(R)}{\mathrm{d}t}\right)^2\right|v\right\rangle \\ &= 2m_e\left\langle v\left|\left(e\frac{\mathrm{d}\langle e|\mathbf{r}|e\rangle}{\mathrm{d}t}\right)^2\right|v\right\rangle \qquad (11)\end{aligned}$$

determines the kinetic energy of the electron charge distribution due to the motion of the nuclei (squared time derivative of electronic coordinate, averaged over nuclear motion). Were the nuclei stationary this term would vanish since

$$i\hbar\frac{\mathrm{d}\langle e|\mathbf{r}|e\rangle}{\mathrm{d}t} = i\hbar\left\langle e\left|\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t}\right|e\right\rangle = \langle e|[\mathbf{r},H]|e\rangle = \langle e|[\mathbf{r},H_{el}]|e\rangle = 0 \qquad (12)$$

It is the motion of the nuclei that prevents the second sum rule from vanishing. The kinetic energy of the nuclei is responsible for the change of the electronic charge distribution during the collision.

The power emitted by a moving dipole is given by $2|\ddot{\mu}(t)^2/3c^3$. Therefore the emission spectrum (units of energy per frequency interval = energy × time) as a function of frequency is given in terms of the dipole function by

$$I(\nu) = \frac{2\omega^4}{3c^3}|\epsilon(\nu)|^2 \qquad (13)$$

where, as discussed in connection with eq 9, $\epsilon(\nu)$ is not quite equal to $\mu(\nu)$ but includes a small quantum correction. The emission spectrum as we compute it for hot clusters can be very well represented by a function of the form[27]

$$I(\nu) = \frac{S_0\beta\exp(-\alpha\beta)}{2}\nu^4\exp(-\beta\nu) \qquad (14)$$

where S_0, α, and β are the first three spectral moments. In particular β can be interpreted as an electronic temperature. α, the quantum correction, is small compared to $1/\beta$ and is the term responsible for the spectrum $|\epsilon(\nu)|^2$ not being a symmetric function of ν over the entire interval $-\infty < \nu < \infty$. At the high electronic temperatures of interest to us α is small compared to $1/\beta$[27] so that $\exp(-\alpha\beta)$ and the spectrum are nearly symmetric.

Equation 11 relates the second moment of the spectrum to the kinetic energy of the electronic charge distribution due to the motion of the nuclei. The second moment is determined by β. For hot clusters it is found that the electronic temperature is 2 orders of magnitude smaller than the nuclear translational temperature. This is not quite surprising considering the fact that the electronic and nuclear degrees of freedom were not allowed to equilibrate as the electrons were restricted to the electronic ground state only.

The power emitted at all frequencies is given by integrating eq 14. By writing the integrand as a function of the dimensionless variable $\beta\nu$ and using $\beta\nu$ as the variable of integration the integrated power is seen to be proportional to β^{-4}. This is what one expects for equilibrium blackbody radiation where the Stefan–Boltzmann law[28] for the energy emitted per unit time and unit area is

$$(\text{power/unit arae}) = \sigma T^4 \qquad (15)$$

The Stefan–Boltzmann constant is $\sigma \cong 5.7 \times 10^{-5}$ erg/(s cm^2 deg^4). This is the first cautionary flag. The electronic temperatures that we obtained [26,27] for impact heated clusters are in the thousands of degrees Kelvin. So T^4 is of the order of 10^{14}–10^{15} and the power emitted per Å^2 by a single hot cluster is of the order of 10^{10} (cm^{-1}/s)/Å^2. While an energy of 10^{10} cm^{-1} is high on the scale of molecular transitions, a power of 10^{10} cm^{-1} is not a lot since the hot cluster survives less than a picosecond before it shatters and all the atoms move apart from one another. Already in the Introduction we raised the possibility that the fleeting existence of the hot cluster does not allow enough time for it to radiate and this is seen to be consistent with the value of the Stefan–Boltzmann constant. We need a longer time window over which emission can take place.

Rather than the emitted energy we can consider the number of emitted photons by dividing the emission spectrum by the energy $\hbar\omega$ per photon and then integrating over all frequencies.

$$\text{number of photons} = \int(h\nu)^{-1}\, I(\nu)\,\mathrm{d}\nu = \frac{32\pi^4}{3hc^3}\int\nu^3|\mu(\nu)|^2\,\mathrm{d}\nu \qquad (16)$$

To make a connection with emission from a macroscopic sample of a mixture of two gases we define $\overline{|\mu(\nu)|^2}$ as the mean spectrum per collision where the averaging is over all impact parameters and relative velocities. Then we can write

$$I(\nu) = \bar{v}\sigma_{\text{eff}}n_{\text{A}}n_{\text{B}}\frac{2(2\pi\nu)^4}{3\pi c^3}\overline{|\mu(\nu)|^2} \qquad (17)$$

where $\bar{v}$ is the averaged relative velocity, σ_{eff} is the effective cross section meaning that the rate of binary collisions (number of collisions per unit volume and unit time) is $\bar{v}\sigma_{\text{eff}}n_{\text{A}}n_{\text{B}}$, and n_{X} is the density of atom X.

In the next section we will determine the mean number of photons emitted by a molecular dynamics simulation. We can obtain an independent value by determining the mean spectrum $\overline{|\mu(\nu)|^2}$ from experiments on mixtures of rare gases[29] by relating the power emitted to the absorption coefficient $\alpha(\omega)$ (dimensions length^{-1}) by[2]

$$I(\omega) = cu(\omega)\,\alpha(\omega) = \frac{\omega^2 kT}{\pi^2c^2}\alpha(\omega) \qquad (18)$$

where $m(\omega)$ is the classical, Rayleigh–Jeans form of the energy density of blackbody radiation.

Molecular Dynamics Simulations

To calculate the collision-induced light emission of hot clusters we used molecular dynamics (MD) simulations of a mixed Ar/Xe cluster impacting a hard surface. The details of the MD are described in refs 26 and 30. Here it is important to note that the dynamics does not allow electronic excitation so that the cluster remains confined to the electronic ground state. The cluster is equilibrated[31] to a temperature of 30 K and then is given a center of mass velocity directed toward a hard wall. The cluster hits the wall, heats by converting the initially directed velocity into a random motion, and fragments in a few hundred femtoseconds after impact. The equations of motion for the atoms are integrated until the interatomic distances are large enough that all dipoles are effectively zero.

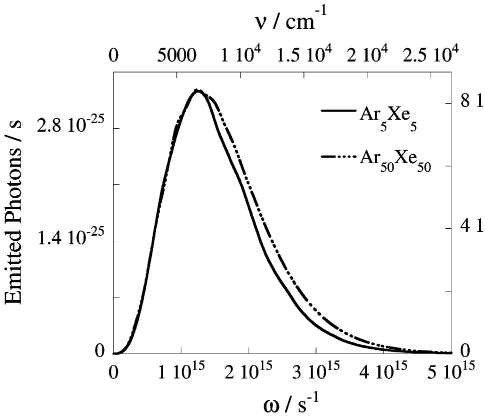

Figure 1. The number of emitted photons per unit frequency [frequency in s^{-1} (lower abscissa) and in wave numbers (upper abscissa)] for a small, Ar_5Xe_5, cluster (ordinate on the left) and a large, $Ar_{50}Xe_{50}$, cluster (ordinate on the right). The impact velocity is 15 km s^{-1}.

The functional form of the Ar−Xe dipole moment function $\mu(R)$ is approximated as[20−22,32,33]

$$\mu(R) = a_0 \exp[-\alpha(R - R_e)] \tag{19}$$

The parameters are $a_0 = 9.321 \times 10^{-3}$au, $\alpha = 6.1714$ Å^{-1}, and $R_e = 2.8707$ Å. The dipole moment of the cluster is taken as the vector sum of the contributions of the dipole of the different mixed pairs. The emission spectrum of the cluster is then computed in terms of the Fourier transform of the dipole moment of the cluster. An alternative way of stating the computational procedure, and a way that allows a closer connection with the theory of collision-induced absorption (or emission[21]) in mixtures is that we first Fourier transform the dipole function for each mixed pair of atoms in the cluster. When we compute $|\mu(\nu)|^2$, the contributions of different dipoles average out and

$$|\mu(\nu)|^2 \approx \sum_{\text{mixed pairs}} |\mu_{\text{pair}}(\nu)|^2 \tag{20}$$

What this means is that the spectrum scales with the number of those mixed pairs that give rise to a significant dipole moment. This is not quite the same as the number of mixed pairs and so, as a practical matter, from the beginning we do not include the contribution from those pairs for which the two atoms never get very near. In a large cluster of N atoms, with a half/half mix of two kinds of atoms, the number of pairs that contribute to the sum in eq 20 scales as $(N/2)^2$ but in a smaller cluster there are definite size effects. As an example, we compared the emission of Ar_7Xe_3 at the same final translational temperature. In equilibrated cold Ar_7Xe_3 there is a Xe core within a half solvation shell of Ar atoms. So some Ar atoms can escape without ever colliding with a Xe atom.

Figure 1 shows the emission spectrum for two different clusters, Ar_5Xe_5 and $Ar_{50}Xe_{50}$, at an impact velocity of 15 km s^{-1}. Because the random part of the kinetic energy after impact scales linearly with the initial energy of impact it follows that the two clusters will reach comparable final temperatures. It is indeed seen that, but for the statistical noise in the results for the small cluster, the two spectra have quite similar widths but the larger cluster emits about 30 times more photons.

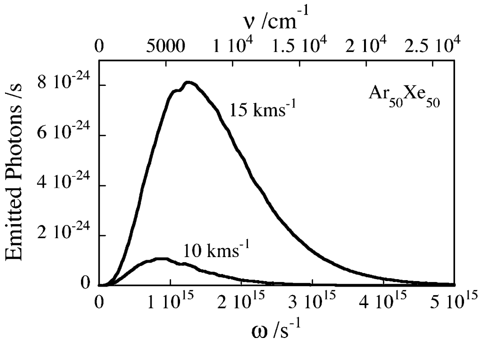

Figure 2. The number of emitted photons per unit frequency at two velocities of impact for the $Ar_{50}Xe_{50}$ cluster.

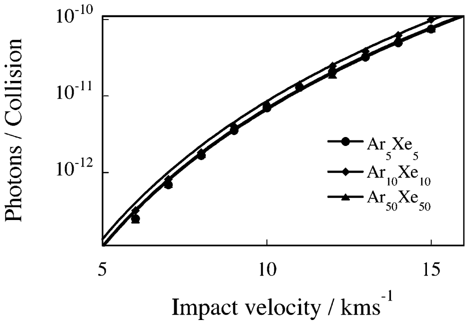

Figure 3. The number of emitted photons per cluster divided by the number of mixed collisions per cluster, logarithmic scale, as a function of the impact velocity, v, for clusters of three different sizes. Points: classical trajectory simulations. Curves: a fit to a v^6 dependence. The dependence of the number of emitted photons on the sixth power is the analogue of the Stefan−Boltzmann dependence of the emitted energy on the eight power, eq 15.

The ordinate in Figure 1 is the number of photons per frequency unit per cluster. The area under the curve is the number of emitted photons per cluster impact. It is seen to be low, of the order of 10^{-10}. This number is strongly increasing with the collision energy as shown in Figures 2 and 3 as follows. First, Figure 2 shows the entire emission spectrum, as in Figure 1 but for two velocities of impact. While it is not clear from this figure, the maximal value scales with the impact velocity to the fourth power while the width scales as the square of the impact velocity. The result is that a very moderate (factor of 1.5) increase in the initial velocity leads to a very significantly more intense and broader spectrum.

For most mixed collisions that take place during the cluster impact, the dipole function is either large or small. So it is possible to define the “number of (mixed) collisions” that occur during the impact by counting the number of terms in eq 20. We can therefore compute the number of photons emitted, on the average, per collision. The results, for clusters of different sizes, are shown in Figure 3. This shows that the number of photons emitted, on the average, per collision is about independent of the cluster size. Figure 3 also shows that the number of emitted photons scales as the sixth power of the impact velocity (or, cf. eq 15, that the emitted energy scales as the eighth power of the velocity).

Collision-Induced Absorption

It follows from eqs 14 and 18 that either the emission or the absorption spectrum has a reduced representation with use of two moments, e.g.,

$$\alpha(\nu) = \alpha_{\max}\alpha^*(\nu^*), \qquad \nu^* \equiv \nu/\nu_{\max} \tag{21}$$

where max means the value at the maximum and the notation is that of Bar-Ziv and Weiss[29] (BZW). These authors showed that eq 21 fits well their (and others) measurements of the absorption coefficient for different mixtures of rare gases at room temperature as well as at lower and somewhat higher temperature. BZW also showed that as a function of temperature $\alpha_{\max}$ scales as T while $\nu_{\max}$ scales as $T^{1/2}$ where T is the translational temperature of the rare gas mixture. We have shown that in cluster impact there is rapid thermalization of the cluster and that our computed spectra for cluster impact satisfies the scaling relations of BZW when we use the translational temperature of the hot cluster.[26,30] (The scaling behavior shown in Figure 3 and the Stefan–Boltzmann law, eq 15, result from the scaling of the translational temperature after the cluster impact with the initial kinetic energy.)

It follows that the measured absorption spectrum of BZW can be extrapolated to high translational temperatures and, using (18), provide the emission spectrum. When we do so the results are quite close to the emission spectrum that we compute from the classical trajectories, showing that the dipole function that we use is realistic.

In addition to elucidating the scaling with the temperature of the mixture, BZW also suggested how the scaling goes with the nature of the two rare gases.

Concluding Remarks

The probability for photon emission in the near-IR/visible regime when two different rare gas atoms collide at a hypersonic velocity was shown to be small, as expected considering the short duration of such a collision and the long radiative times in the near-IR. The yield of photons increases dramatically with temperature satisfying a Stefan–Boltzmann T^4 type law. There are three alternatives for increasing the number of photons per cluster. One is the obvious option of using larger clusters whereby the number of heteroatom collisions increases with size, Figure 1. Two other options are either to collisionally induce an otherwise symmetry forbidden molecular transition or to collisionally induce energy transfer to molecular modes that can emit also after and not only during the collision.

Acknowledgment. Our computational results can also be checked by using our dipole function, eq 19, to compute directly the two moments of the collision-induced absorption spectrum of a thermal mixture. We are very grateful to David Reguera and George Birnbaum who have carried out such a computation. This work was supported by the Air Force Office of Scientific Research and by the EU network on cluster cooling.

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