Thermal radiation from small particles

K. Hansen[*,1,2] and E. E. B. Campbell[1,3]

[1]Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Postfach 1107, D-12474 Berlin, Germany
[2]Institute of Physics and Astronomy, University of Aarhus, Ny Munkegade, Bygn. 520, DK-8000 Aarhus C, Denmark
[3]School of Physics and Engineering Physics, Gothenburg University and Chalmers University of Technology,
S-41296 Gothenburg, Sweden

We derive an expression for the emission of electromagnetic radiation from small, highly excited, and isolated particles in a cold environment. The result is a generalization of Planck's blackbody formula on two counts. One is due to the finite level densities of small particles. It is most pronounced for very small particles and for high photon energies. The other effect is the absence of stimulated emission which influences the low-energy part of the spectrum. We discuss some consequences for the interpretation of experimental emission spectra. [S1063-651X(98)03211-5]

PACS number(s): 05.70.−a, 44.40.+a, 36.40.−c, 95.30.Jx

INTRODUCTION

Thermal radiation has had a profound significance on the development of modern physics [1] and is one of the fundamental processes in nature. It has an importance that spans a very large range of physical systems, from astronomical and cosmological questions to the more specialized but related discipline of thermal radiation from small particles. The latter has recently been the object of laboratory experiments which demonstrated thermal radiation from small particles as well as from clusters and molecules [2–5]. Also the influence of radiative cooling on unimolecular reaction rates has been studied, mainly in fullerene molecules [6–9].

The radiation spectra have all been interpreted in terms of Planck radiation, modified by a spectral emissivity which depends on both the wavelength of the light and the dimension of the particle [10] in a nontrivial extension of the optical properties of macroscopic bodies to microscopic sizes. In this paper we consider how the Planck radiation itself must be generalized in order to describe the radiation from small particles, a generalization which goes beyond the modifications due to the emissivity. In the situations described in [2–5], the radiation will be shown to have a form different from the usual radiation law of a Planck expression corrected by an emissivity. For sufficiently small particles, not only the spectral emissivity differs from bulk values, but the radiation will also be influenced by the finite number of degrees of freedom of the particles.

OPTICAL EMISSION FROM SMALL, ISOLATED PARTICLES

As in the case of the spectral emissivity corrections, the modifications can be traced to the finite size of the particle. They apply to small particles that only exchange energy with the surroundings through emission of radiation. The derivation will follow the one given by Einstein [11] and gives the spectral emission in terms of optical and energetic properties of the particles. Although the results are derived with molecular beam experiments in mind, they are generally applicable to radiation from small, isolated, and highly excited particles in a radiative cold environment. These particles will also be assumed to exhibit a strong statistical mixing of states, so that the emission rate and the frequency of the emitted light is independent of the way the energy is originally deposited into the particle. This implies that the radiative lifetime is much longer than the time needed to exchange energy between two quasistationary states. Even for very small particles, the evidence obtained so far argues strongly in favor of this ordering. The emission spectra measured in [2–5] are surprisingly similar considering the very different preparation methods; they range from pulsed laser desorption of carbon molecules to chemical oxidation of transition-metal clusters.

The emitted radiation from small, isolated particles is changed compared to macroscopic radiation for four different reasons: (i) The finite linear size of the particles influences the spectral emissivity (see [10]), as mentioned above, (ii) the related but different phenomenon of a limited heat capacity, (iii) the fact that the radiation occurs at specified energy as opposed to constant temperature, and finally (iv) that the particles emit the radiation without the presence of any appreciable blackbody radiation from the surroundings.

The finite-size effects of the emissivity mentioned under (i) are **not** the subject of this paper and we will not go into details with the subject but simply apply the results whenever needed. Let us just mention that the theory relates the absorption efficiency, Q_{abs}, of the very small particles in, e.g., [4,5] (on the order of 100 atoms) to the ratio of the particle radius r and the wavelength of the emitted photon λ and to a function of the complex index of refraction, m. Q_{abs} is defined as the ratio between the actual photon absorption cross section and the geometric one,

$$\sigma_{abs} \equiv Q_{abs} \pi r^2. \tag{1}$$

Under certain conditions the relation attains a particularly simple form [10]:

*Electronic address: klh@dfi.aau.dk

$$Q_{abs} = \frac{8\pi r}{\lambda} \, \mathrm{Im}\left(\frac{m^2-1}{m^2+2}\right). \tag{2}$$

This expression was used in [4,5] with m constant. To the extent this simplified expression holds, one sees that the absorption cross section is proportional to the volume of the particle or, in other words, to the number of atoms composing the particle. In the spectral regions where m behaves reasonably, i.e., away from resonances, Q_{abs} is small compared to one by a factor of typically r/λ and the absorption cross section is similarly suppressed.

A small absorption efficiency, on the other hand, implies an equally small emissivity. A small emissivity is important in conjunction with the absence of background radiation. Since the surroundings are much colder than the particle, the radiation from the exterior is negligibly small. If also the emission from the particle is suppressed, the result is that little radiation is present at all to stimulate radiation from the particle. The consequence is that stimulated emission is practically absent. The amount to which this reduces the radiant energy is found by thermal equilibrium considerations. In thermal equilibrium, the ratio of spontaneous to total emitted energy at frequency ν is equal to

$$\frac{A_m^n}{A_m^n + \rho B_m^n} = 1 - e^{-h\nu/k_BT}, \tag{3}$$

independent of the properties of the initial and final states m and n. Here, ρ is the thermal equilibrium radiation energy density. The optical constants A_m^n and B_m^n (and B_n^m, used below) are defined as in [11]. The radiation from optically thin particles at temperature T but in a radiationless environment is therefore reduced by this factor as compared with the macroscopic blackbody expression.

This conclusion only holds if the particle emits an amount of radiation insufficient to provide any significant background radiation density. It is possible to get an estimate as to whether the particle size exceeds this limit if a part of the emission spectrum is known. The estimate is simplest if the emission spectrum is smooth with no strong features. This is indeed the case for the spectra of [2–5]. Consider first the effect emitted in thermal equilibrium at a given frequency, ν. It is of the order $\sigma\rho cd\nu$, where σ is the absorption cross section and ρ is still the equilibrium radiation density. The energy is emitted in a volume of the order of λ^3 where it resides for time of the order of λ/c. This gives an energy density on the order of $\sigma\rho cd\nu\lambda/c/\lambda^3 = \rho d\nu\sigma/\lambda^2$. Since the equilibrium value is $\rho d\nu$, the emission gives a background radiation on the order of σ/λ^2 of the equilibrium value.

An upper limit for σ is then found combining the measured spectra and sum rules. The energy integrated absorption cross section is given by the number of valence electrons in the particle, N [12]:

$$\int_0^\infty \sigma \, dE = \frac{e^2}{4\pi\epsilon_0} \frac{2\pi^2\hbar}{cm_e} N. \tag{4}$$

The right-hand side of this is evaluated to 1.098 eV Å^2N. A lower limit of the integral can also be estimated in terms of an average cross section using the experimental curves. These are quite smooth with the implication that σ is fairly constant over the spectral range covered. Then the integral is on the order of $\sigma_{av}\Delta E$, where σ_{av} is the average cross section in the wavelength region and ΔE is the photon energy interval spanned in the experiment. ΔE is typically 2–3 eV. Thus

$$\int_0^\infty \sigma \, dE > \sigma_{av}\Delta E. \tag{5}$$

Then the cross section σ_{av} is limited by

$$\sigma_{av} < 1.098 \text{ eV Å}^2N/\Delta E \sim 0.5 \text{ Å}^2N. \tag{6}$$

The ratio of radiation energy densities to the thermal equilibrium densities is then evaluated to be less than $0.5 \text{ Å}^2N/\lambda^2$. Since N is the number of valence electrons in the particle which ranges from a few hundred to a few thousand and λ^2 is on the order of 10^7 Å^2, the ratio is orders of magnitude smaller than 1, at least in the cases of [5,4] where particle sizes are known. Hence the radiation from the particles does not stimulate any emission.

It is useful to have an explicit expression for the photon emission rate in the absence of background radiation but for a given temperature. It is derived using the relation [11]

$$p_m A_m^n = \frac{8\pi h\nu^3}{c^3} p_n B_n^m, \tag{7}$$

where p_n, p_m are the degeneracies for the states n and m with energies E_n and E_m, respectively. We are concerned with averages and sums over states n,m with a constant difference in energy of $h\nu$. The thermal average is thus over all initial states, populated with the proper statistical weights, and the sum is over all final states with appropriate energy. The thermally averaged emission/absorption rates per frequency interval are then, with Z the partition function,

$$\langle A'\rangle \equiv \frac{1}{Z}\sum_{m,n} A_m^n p_m e^{-E_m/k_BT}\delta\left(\frac{E_m-E_n}{h}-\nu\right),$$

$$\langle B'_{abs}\rangle \equiv \frac{1}{Z}\sum_{m,n} B_n^m p_n e^{-E_n/k_BT}\delta\left(\frac{E_m-E_n}{h}-\nu\right), \tag{8}$$

$$\langle B'_{emis}\rangle \equiv \frac{1}{Z}\sum_{m,n} B_m^n p_m e^{-E_m/k_BT}\delta\left(\frac{E_m-E_n}{h}-\nu\right).$$

The relation Eq. (7) yields

$$\frac{8\pi h\nu^3}{c^3}\langle B'_{abs}\rangle Z = \frac{8\pi h\nu^3}{c^3}\sum_{m,n} p_n B_n^m e^{-E_n/k_BT}\delta\left(\frac{E_m-E_n}{h}-\nu\right)$$

$$= \sum_{m,n} A_m^n p_m e^{-E_n/k_BT}\delta\left(\frac{E_m-E_n}{h}-\nu\right)$$

$$= e^{h\nu/k_BT}\langle A'\rangle Z, \tag{9}$$

where the last equality simply follows from the fact that $E_m = E_n + h\nu$. Thus the relation

$$\langle A'\rangle = \langle B'_{abs}\rangle \frac{8\pi h}{c^3}\nu^3 e^{-h\nu/k_BT}. \tag{10}$$

The prime indicates that the averages are differential quantities with units as the coefficients per frequency interval. This should be compared to the more familiar result which includes stimulated emission:

$$\langle A \rangle + \rho \langle B_{emis} \rangle = \langle B_{abs} \rangle \frac{8\pi h}{c^3} \nu^3 \frac{e^{-h\nu/k_BT}}{1-e^{-h\nu/k_BT}}. \quad (11)$$

The result in Eq. (10) pertains to a situation where thermal equilibrium is established by means other than radiation but is nevertheless present. Often particles are isolated as, for example, in molecular beam experiments. Such particles must be described as a microcanonical system, i.e., they possess a certain internal energy rather than a temperature. With the absence of a temperature, Planck's radiation law cannot be valid in the canonical form and a replacement must be found. These rules can be found by application of the relation in Eq. (7). By the hypothesis of strong statistical mixing, a state of the radiating particle is specified by conserved quantities: the energy, the angular momentum, and the momentum. Hence the relevant quantity for characterizing the radiation from the particles in the case of strong statistical mixing is the average over all microstates with the same values of these conserved quantities. In other words, we can describe the radiation from a molecule with given values of the conserved quantities by a single set of Einstein coefficients. The problem reduces further, since neither conservation of linear nor angular momentum effects the emission rates much. The first implies a correction on the order of the Doppler shift. Angular momentum is potentially more relevant since the photon itself carries one quantum. However, the rotational constants of most molecules are so small that the levels are spaced much more densely than the average photon energy. Even applying selection rules, the absorption and emission can be considered as a continuous function of energy. Hence only the internal energy need be considered when specifying the state of the molecule. The degeneracies p_n and p_m can then be replaced by the level densities at the corresponding energies, $p(E_n)=p(E_m-h\nu)$ and $p(E_m)$.

A formal derivation proceeds as follows: The relation [12]

$$\sigma_n^m \frac{c}{h\nu} = B_n^m \delta\left(\frac{E_m-E_n}{h}-\nu\right) \quad (12)$$

combined with Eq. (7) yields

$$\sum_m p_m A_m^n \delta\left(\frac{E_m-E_n}{h}-\nu\right) = \frac{8\pi\nu^2}{c^2} p_n \sum_m \sigma_n^m \equiv \frac{8\pi\nu^2}{c^2} p_n \sigma_n, \quad (13)$$

where σ_n is the total cross section at frequency ν from state n, $\sigma_n = \sum_m \sigma_n^m$. Using the statistical mixing ansatz, we can replace the remaining sum over emitting states m with an integral,

$$\frac{8\pi\nu^2}{c^2} p_n \sigma_n = \int_0^\infty dE_m p(E_m) A^n(E_m) \delta\left(\frac{E_m-E_n}{h}-\nu\right)$$

$$= hp(E_n+h\nu)A^n(E_n+h\nu), \quad (14)$$

where $A^n(E_m)$ is the emission coefficient from energy $E_n+h\nu$ into state n. Summing over all n states in the small

energy interval δE_n replaces $\sigma_n p_n$ with the interval average $\sigma(E_n)$ through $\Sigma_n \sigma_n p_n = \sigma(E_n)p(E_n)\delta E_n$. Thus

$$\frac{8\pi\nu^2}{c^2} \sigma(E_n)p(E_n)\delta E_n = hp(E_n+h\nu)\sum_n A^n(E_n+h\nu), \quad (15)$$

where the sum on the right-hand side is over the states n in the energy interval δE_n. Since the frequency interval is $\delta\nu = \delta E_n/h$, the photon emission rate per frequency interval A',

$$A'(E_n+h\nu)\delta\nu \equiv \sum_n A^n(E_n+h\nu), \quad (16)$$

is then given by

$$A'(E) = \frac{8\pi\nu^2}{c^2} \sigma(E-h\nu) \frac{p(E-h\nu)}{p(E)} \quad (17)$$

when $E \equiv E_m = E_n + h\nu$. This is the microcanonical, small particle analog of the well known Planck radiation law in Eq. (11).

It is interesting to note that Eq. (17) is similar to the angular momentum averaged Weisskopf expression for neutron emission from hot nuclei [13], an expression that has also been applied to unimolecular reaction rates. The difference is that the activation energy for photons is zero and the level density due to the motion of the fragment is replaced by the level density of the photon, i.e., the electromagnetic mode density. The similarity of the two expressions is rooted in the similar starting points, viz., detailed balance considerations. Although the close correspondence is not surprising, it is nevertheless gratifying.

Previously Dunbar *et al.* and Allamandola *et al.* have derived microcanonical expressions for thermal radiation from molecules [14,15]. These solutions contain some of the same elements as ours, mainly the finite heat bath effects introduced through the level density. The main limitation of these results is that only the vibrational $\Delta v=1$ transitions are considered. This limits these results to the infrared part of the spectrum which can therefore not account for emission of the much more energetic visible and ultraviolet radiation observed in, e.g., [5,4].

The difference between the canonical Planck (Mie) radiation law and ours is most pronounced in the extremes of the spectrum. Comparing first the two canonical versions of the radiation law, Eqs. (11) and (10), the correction for absent stimulated emission is given by the factor $1-e^{-h\nu/k_BT}$, which is approximately $h\nu/k_BT$ for small photon energies and negligible for large photon energies. To be specific, let us take the Q_{abs} of Eq. (2) to be proportional to ν, corresponding to a frequency-independent dielectric function. The Mie-Planck expression for the emitted energy density

$$P(\nu)d\nu \propto \nu^4(e^{h\nu/k_BT}-1)^{-1}d\nu$$

$$\approx \nu^3 k_B T e^{-h\nu/k_BT}d\nu \quad (h\nu \ll k_BT) \quad (18)$$

will instead be

$$P(\nu)d\nu \propto \nu^4 e^{-h\nu/k_BT}d\nu \quad (h\nu \ll k_BT). \quad (19)$$

The total emitted energy, however, will only be reduced by the modest factor of Riemann's ζ function with argument 5, $1/\zeta(5)=1/1.0369...$.

Much more important are the differences at high photon energy. The two expressions Eqs. (17) and (10) differ at high photon energies due to the finite level density of the particles. A particle with a level density $p(E) \propto (E+E_0)^{C_v-1}$ and the derived high-temperature caloric curve $E=C_v k_B T - E_0$ emits radiation with the spectral distribution

$$P(\nu)d\nu = Ah\nu\, d\nu \propto \nu^4 \left(1-\frac{h\nu}{E+E_0}\right)^{C_v-1} d\nu. \quad (20)$$

With the microcanonical temperature T_m,

$$T_m = \left(\frac{d\,\ln(p(E))}{dE}\right)^{-1} = \frac{E+E_0}{C_v-1} \approx \frac{E+E_0}{C_v}, \quad (21)$$

the emitted energy density becomes

$$P(\nu)d\nu \propto \nu^4 \left(1-\frac{h\nu}{k_B T_m C_v}\right)^{C_v-1} d\nu. \quad (22)$$

This can be approximated by [16]

$$P(\nu)d\nu \propto \nu^4 \exp\left(-\frac{h\nu}{k_B T_m}-\frac{1}{2C_v}\frac{(h\nu)^2}{(k_B T_m)^2}\right)d\nu. \quad (23)$$

The finite-size correction is summarized in the second-order term in the exponent. It is analogous to the finite heat bath effect discussed by Klots but it differs from it due to its energy dependence. Since the photon energy varies from zero to several eV, the equivalent temperature of the theory is not a constant but varies with the emission channel. To the same precision as previously, the emitted energy density becomes

$$P(\nu)d\nu \propto \nu^4 \exp\left(-\frac{h\nu}{k_B T_m - h\nu/2C_v}\right)d\nu. \quad (24)$$

Whereas the frequency-integrated radiated energy is only reduced by a factor of approximately $(1-6/2C_v)^5$ compared to Eq. (10), the distortion of the spectrum in the visible and the uv region where optical measurements are usually performed is significant. Corrections for a frequency dependence of the emissivity other than the $1/\lambda$ used here is easily made in the results here.

CONSEQUENCES FOR THE ANALYSIS OF EXPERIMENTS

In order to apply Eq. (17) to interpret experimental spectra, one must take into account the distribution of energies carried by the molecules. In general, this must be done by integrating Eq. (17) over the energy distribution but for sufficiently narrow distributions this can be done approximately and expressed in terms of the first two moments of the distribution. Parametrizing the distribution by a Gaussian,

$$f(E)dE \propto \exp(-(E-E_g)^2/2\sigma_E^2), \quad (25)$$

leads by a saddle-point expansion to the result, valid to leading order in $1/C_v$ and $\sigma_E/(E_g+E_0)$,

$$P(\lambda)d\lambda \propto \lambda^{-6}\exp\left[-\frac{hc}{\lambda k_B T_m}+\frac{a}{2C_v}\left(\frac{hc}{\lambda k_B T_m}\right)^2\right]d\lambda, \quad (26)$$

where the coefficient a is defined as

$$a = \frac{C_v \sigma_E^2}{(E_g+E_0)^2}-1. \quad (27)$$

This relation incorporates the two preceding cases ($a=-1$ for microcanonical and $a=0$ for canonical).

Obviously the value of a depends on the method used to prepare the ensemble in a given experiment. But it is possible to give the asymptotic value of a, i.e., the value after a sufficient number of photons has been emitted. Upon photon emission the width of the energy distribution is increased by the spread in photon energies and by the fact that emissions occur statistically in time. This increases the variance of the energy distribution during one typical photon emission time from σ_E^2 to $\sigma_E^2 + \sigma_{h\nu}^2 + \langle h\nu \rangle^2$. The first is the variance of the individual photon energies, approximately $\langle h\nu \rangle^2/(n+1)$ for a radiation law $P(\nu)d\nu \propto \nu^n p(E-h\nu)/p(E)d\nu$. The second is the variance in energy due to the distribution in the number of emitted photons. After the emission of the average of one photon, the variance in the number is also 1, assuming Poisson statistics. Then the variance in energy is simply the average photon squared, $\langle h\nu \rangle^2$. On the other hand, the width of the distribution is reduced because the most highly excited molecules have a higher emission rate. Hence the high-energy side of the distribution will lose energy faster than the low-energy side, effectively compressing the distribution. We can estimate this compression if we note that the energy distribution $f(E)$ with width σ_E^2 is changed to

$$f\left[E+\langle h\nu \rangle\left(\frac{T_m}{T_g}\right)^{n+1}\right] \quad (28)$$

when on the average one photon is emitted. T_g is the microcanonical temperature corresponding to the average energy. The last term in the argument accounts for the energy dependence of the photoemission rate. Expanding the argument to first order in the energy and using that $\langle h\nu \rangle = (n+1)T_g$, we see that the energy scales with the factor $1+(n+1)^2/C_v$. Provided this is close to 1, i.e., for not too small heat capacities, the variance will then scale with $1+2(n+1)^2/C_v$. Hence the variance will be compressed with the term $-2(n+1)^2\sigma_E^2/C_v$. For an average photon emission of energy $\langle h\nu \rangle$, the total change of the variance is then

$$\Delta\sigma_E^2 = \frac{\langle h\nu \rangle^2}{n+1}+\langle h\nu \rangle^2 - 2(n+1)^2\frac{\sigma_E^2}{C_v}. \quad (29)$$

Since $\langle h\nu \rangle = (n+1)(E_g+E_0)/C_v$, the stationary point of this equation is given by

$$\sigma_E^2 = \frac{(E_g+E_0)^2(1+1/(n+1))}{2C_v} \approx \frac{(E_g+E_0)^2}{2C_v} = T_m^2 C_v/2. \quad (30)$$

This is less than the canonical variance by a factor 2. One will retrieve the canonical value if exposing the particle to an

equilibrium radiation field: The first two terms in Eq. (30) are doubled since absorption is as frequent and will induce the same changes as emission.

The variance on the energy distribution given in Eq. (30) is identical to the one pertaining to an evaporative equilibrium for large clusters [17]. The reason is the shared feature that the emission rates in both cases only change moderately for two consecutive decays. For the asymptotic situation the a parameter of Eq. (17) is then equal to $-\frac{1}{2}$. This should be compared to the microcanonical and isoenergetic value $a = -1$ and the canonical value of $a = 0$. The number of photon emissions needed to reach the asymptotic value is on the order of $C_v/2(n+1)^2$, which for, e.g., C_{60} is 2–3 when $n = 5$. These results are radiative analogs of results derived for the evaporative ensemble [17,18] and constitute the basics of a radiative ensemble based on statistical, thermal radiation. By comparison with [17] we see that an important effect is to replace the evaporative Gspann parameter by the quantity $\sqrt{2}(n+1)$ which is generally smaller.

We have refitted the data of [5], which show the light emitted from laser desorped C_{60}. The data were fitted by the authors to an energy density function of the Planck-Mie form with a constant dielectric constant,

$$P(\lambda)d\lambda \propto \lambda^{-6}(1 - e^{-hc/\lambda k_B T})^{-1}d\lambda, \qquad (31)$$

with the results $T = 2540$, 2570, 2950, and 2380 K. We used Eq. (26) and a version of Eq. (17) based on the emissivity of a metallic sphere [9]. The latter increases the frequency dependence by a factor ν compared to Eq. (17) and was suggested to account for the radiative cooling of C_{60} anions. Both gave significantly reduced fitted temperatures and also a reduced spread in the values. The values are, in the same order, 2020, 1800, 1820, and 1790 K for Eq. (26) and 1750, 1590, 1610, and 1500 K for the metallic version of Eq. (17). The relative difference in fitted temperature is approximately $1/n$ as expected. The values of a are quite similar for all fits in both cases (2.8, 3.7, 4.5, and 3.0) and (2.9, 3.4, 4.1, and 3.2) corresponding to a width on the energy distribution which is about a factor 2 bigger than the canonical value. It was not possible to distinguish between the two different emissivities from the quality of the fit but the systematic undershoot at small wavelengths in [5] has disappeared.

The positive value of a indicates that the molecules in these experiments are desorbed with an energy distribution which is broader than canonical and have not reached the asymptotic value of the radiative ensemble. This is confirmed by a comparison of the observation time of [5] (10 μs) with the absolute cooling rate for C_{60} anions which, when converted to a temperature of 1700 K, gives an average photon emission rate of 0.5 ms^{-1}. A similar rate (0.3 ms^{-1}) is obtained if the relatively low temperature gas phase absorption cross section [19–21] is inserted into Eq. (17) and a ν^3 behavior of the cross section is assumed, consistent with the power law fitted in [9]. For the latter estimate the literature values of the cross sections at $\lambda = 330$ nm were averaged to 2 Å^2 and the peak structure in the absorption seen in [20,21] was assumed to have disappeared at the higher temperatures that are relevant here. In view of the uncertainties in the absorption cross section, the two rates agree very well. The conclusion is that the emission spectra probe the energy distribution as produced during the desorption. Provided a realistic dielectric function is available, spectra of this kind can then be used to obtain information on the desorption process itself.

CONCLUSION

We have derived an expression for the emission of light from small and highly excited particles. The expression is analogous to formulas for unimolecular decay rates due to the common feature of a limited heat capacity and the absence of stimulated emission. The formula is applied to experimental spectra of laser desorbed C_{60}. We find that the desorbed material has an energy distribution which is wider than a canonical distribution and that the width is created during the desorption process and not during the subsequent radiative cooling.

ACKNOWLEDGMENTS

[1] M. Planck, *Wärmestrahlung* (1914), translated in *The Theory of Heat Radiation* (Dover, New York, 1991).

[2] E. A. Rohlfing, J. Chem. Phys. **89**, 6103 (1988).

[3] R. Scholl and B. Weber, in *Physics and Chemistry of Finite Systems: From Clusters to Crystals*, Vol. 374 of NATO Advanced Study Institute Series C: Physics (Kluwer Academic, New York, 1992), p. 1275.

[4] U. Frenzel, A. Roggenkamp, and D. Kreisle, Chem. Phys. Lett. **240**, 109 (1995).

[5] R. Mitzner and E. E. B. Campbell, J. Chem. Phys. **103**, 2445 (1995).

[6] E. Kolodney, A. Budrevich, and B. Tsipinyuk, Phys. Rev. Lett. **74**, 510 (1995).

[7] K. Hansen and E. E. B. Campbell, J. Chem. Phys. **104**, 5012 (1996).

[8] J. Laskin, J. M. Behm, K. R. Lykke, and C. Lifshitz, Chem. Phys. Lett. **252**, 277 (1996).

[9] J. U. Andersen, C. Brink, P. Hvelplund, M. O. Larsson, B. Bech Nielsen, and H. Shen, Phys. Rev. Lett. **77**, 3991 (1996).

[10] C. F. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles* (Wiley, New York, 1983).

[11] A. Einstein, Z. Phys. **18**, 121 (1917), reprinted in *Sources of Quantum Mechanics*, edited by B. L. Van der Waerden (Dover, New York, 1967).

[12] H. Friedrich, *Theoretical Atomic Physics* (Springer-Verlag, Berlin, 1991).

[13] V. Weisskopf, Phys. Rev. **52**, 295 (1937).

[14] R. C. Dunbar, J. Chem. Phys. **90**, 7369 (1989).

[15] L. J. Allamandola, A. G. G. M. Tielens, and J. R. Barker, Astrophys. J., Suppl. Ser. **71**, 733 (1989).

[16] S. Frauendorf, Z. Phys. D **35**, 191 (1995).

[17] U. Näher and K. Hansen, J. Chem. Phys. **101**, 5367 (1994).

[18] C. E. Klots, J. Phys. Chem. **92**, 5864 (1988).

[19] Brian B. Brady and Edward J. Beiting, J. Chem. Phys. **97**, 3855 (1992).

[20] Qihuang Gong, Yuxing Sun, Ziwen Huang, Xihuang Zhu, Z. N. Gu, and Di Qiang, J. Phys. B **27**, L199 (1994).

[21] C. E. Coheur, M. Carleer, and R. Colin, J. Phys. B **29**, 4987 (1996).